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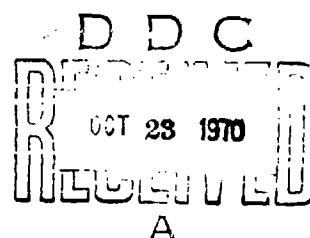
## STABILITY AND COMPATIBILITY STUDIES ON ADVANCED ROCKET PROPELLANT COMPONENTS

Ivan C. Smith  
Raymond E. Foscante  
John W. Nebgen  
A. D. McElroy  
Midwest Research Institute

### FINAL REPORT

Contract No. FO4611-68-C-0011

July 1970



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#### FOREWORD

This research program was conducted for the Air Force Rocket Propulsion Laboratory, Edwards Air Force Base, California by Midwest Research Institute, 425 Volker Boulevard, Kansas City, Missouri 64110. The program was conducted in the Physical Sciences Division. Dr. A. E. McElroy, Head of the Inorganic Chemistry Section was the program supervisor and Dr. Ivan C. Smith, Principal Chemist, was project leader.

Personnel who contributed to this program included: Dr. J. W. Nebgen, Dr. T. W. Lapp, Dr. R. E. Foscante, Dr. W. V. Best, Dr. J. J. Downs, Mr. N. Stich, Mr. Y. Mizumoto, and Mrs. C. Weis.

The Air Force Project Engineer from program initiation date through June 1969 was Capt. R. E. Foscante, and from June 1969 to the end of the contract, Capt. D. F. Clark, RPCS, AFRPL.

This research was conducted under Contract No. F04611-68-C-0011 (Midwest Research Institute Project No. 3100-C). The technical effort on this project covered the period 1 July 1967 to 1 April 1970.

This report covers all the work conducted during this program including that previously reported in AFRPL-TR-68-96, AFRPL-TR-68-183, AFRPL-TR-69-217, the monthly letter reports and some special reports. This report is written in a manner so as to eliminate the need for retention of previous reports.

Publication of this report does not constitute Air Force approval of the report's findings and conclusions. It is published only for the exchange and stimulation of ideas.

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ABSTRACT

(C) A number of candidate advanced propellant ingredients were studied with the objective of obtaining definitive information regarding their usefulness in new propellant systems. The research was laboratory based, involved small quantities (generally less than 100 mg.) of the ingredient, and dealt generally with the stability of individual ingredients and with stability-compatibility of two or more components of proposed propellants.

(C) The ingredients studied include:

Perchlorates--HAP, HP-2, DOAP and AP (for comparison),

N-F Materials--PBEP, TVOPA and P-722,

Fuel--AlH<sub>3</sub>, and

Numerous state-of-the-art binder prepolymers and curatives.

(C) The results of this study, in combination with data produced elsewhere on related programs, yielded the following picture of ingredient potential and problems.

(C) HP-2 - inherent properties of this oxidizer pose serious difficulties for which no solution is apparent.

(C) HAP - nominally more tractable than HP-2, this oxidizer has fundamental properties which translate into problems for the propellant formulator, and have cooled enthusiasm for its use.

(C) DOAP - the first few samples of this very new oxidizer were disappointing in stability and compatibility. Improvements are possible.

(C) P-BEP - a very difficult substance in the quality control sense; apparently fundamentally unstable in practice, a feature not readily understood in theory and likely due in large part to the impurity-structure defects of production samples.

(C) P-722 and TVOPA - stable and compatible, with only minimal reservations.

(C) AlH<sub>3</sub> - needs to be better understood, its quality and reproducibility controlled; use hinges on improvement in these areas.

(C) Scavenger and stabilizer studies relative to AlH<sub>3</sub> and P-BEP are encouraging to date, and comprise a part of the basis for optimism about these substances.

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I.

## **INTRODUCTION**

Midwest Research Institute initiated this program in 1967 under Air Force Contract No. F04611-68-C-0011 to study the stability and compatibility of propellant ingredients. These studies were designed to yield information which would be used to determine propellant processing limitations and to identify reactions between ingredients which might have deleterious effects during storage and aging of these propellants.

This report covers all the work conducted under this contract, including the following subjects: Experimental Procedures, Oxidizers, NF-Materials, Aluminum Hydride and Stabilizers. A topical summary is given at the end of each section and major findings are synopsized in the Summary and Conclusions, Section III.

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II.

## **PROGRAM OBJECTIVES**

The objectives and purpose of this program were to:

1. Assess the stability and compatibility of energetic ingredients being considered for use in advanced propellants, in laboratory scale studies employing techniques and instrumentation not easily applied in larger scale programs. Flexibility was maintained within the program so that the techniques and capabilities could be used to evaluate new ingredients developed during the program.
2. Develop improved techniques for measuring the stability and compatibility of propellant ingredients and to use such information as input data in assessing whole propellant storage life and aging characteristics.
3. Develop practical methods to improve ingredient properties in order to eliminate or circumvent propellant storage problems.

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III.

SUMMARY AND CONCLUSIONS

(U) This program was started in mid-1967. At that time several advanced propellant ingredients were being actively studied, in research and development programs characterized by a considerable sense of urgency to develop rocket motors suitable for weapons systems. In mid-1967 these programs were generally experiencing difficulties attributable to the energetic nature of the ingredients and to the lack of propellant formulation technology for advanced ingredients.

(U) A firm basis for assessing the potential of various advanced ingredients did not exist; the industry looked primarily to development and production programs for both the facts with which to appraise the value of ingredients and for means for solving stability problems. The purpose of the program described herein was to provide supporting data, laboratory derived, useful for definitive appraisals of advanced ingredients, for delineation of problems, and for derivation of solutions to problems.

(C) Three classes of advanced ingredients investigated during this program were: (1) perchlorate salts, (2) difluoramino compound, and (3) the energetic fuel aluminum hydride. HAP, HP-2 and DGAP were the perchlorates investigated on the program. Representatives of the difluoramino class studied on the program are P-BEP, TVOPA, and P-722. The advanced fuel was AlH<sub>3</sub>.

(C) As of this writing, all but one (perhaps two) of the above advanced ingredients are still under consideration. The status of each ingredient can be generally summarized as follows:

Perchlorate Salts

(U) HP-2 is the clear cut casualty. It is not now under consideration in advanced systems. Revived interest will require a major breakthrough, such as a perchloric acid suppressor-scavenger.

(C) HAP is more subtle in its perversity than is HP-2, and by some yardsticks would seem to be a worthy candidate for continuing development. However, laboratory observed peculiarities of HAP seem to carry through faithfully to bench and pilot scale operations. The nature of the difficulties is such that interest in HAP would increase if, for example, a well documented discovery of the beneficial removal of an impurity occurred.

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(C) DQAP was too new and too variable in purity to be definitively evaluated on this program. This quite interesting compound thus is the subject of continuing studies elsewhere.

### Difluoramino Compounds

(C) P-BEP is a surviving candidate, subject both to continuing review and to efforts to obtain practical basic information needed for further development. The future of this ingredient appears to hinge on development of suitable HF scavengers or perhaps through mutual stabilization by other ingredients such as  $\text{AlH}_3$ .

(C) TVOPA and P-722 are C-N-F based plasticizers. Both remain as candidate advanced ingredients, perhaps the best of the lot from the points of view of inherent stability and compatibility with other ingredients.

### Advanced Fuel

(C) The status of  $\text{AlH}_3$  is much like that of P-BEP:  $\text{AlH}_3$  is needed; it poses problems which are not simple; and basic and practical information about  $\text{AlH}_3$  is a requirement. The hydrogen evolution problem does not appear to be one of inherent instability but instead a problem of surface reactivity.

(C) A tremendously complicating factor in the evaluation of advanced propellant ingredients arises from the fact that substantial steps forward in performance require more than one advanced ingredient in a propellant. Thus, P-BEP and  $\text{AlH}_3$  is an attractive combination, and P-BEP-HAP- $\text{AlH}_3$  is even more attractive. It does not necessarily hold that individual faults are additive (or worse) in multi-advanced ingredient systems; however, one does not usually anticipate that two shortcomings will nullify one another. We have seen examples of both effects. HAP is relatively stable (innocuous) by itself and in the presence of conventional propellant ingredients, but does not get along well with either P-BEP or  $\text{AlH}_3$ . P-BEP and  $\text{AlH}_3$  actually seem to improve one another--for the present, they comprise an unusual mutual admiration society.

(U) The usefulness of each ingredient must be assessed in terms of both its inherent stability and its compatibility with other ingredients. The following sections describe the characteristics of the advanced ingredients in these terms.

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## **A. Stability**

(U) On the basis of stability, the ingredients can be described as follows:

(C) HAP and HP-2 do not measure up to AP in stability, but they are stable enough, by themselves, to survive ordinary temperatures of cure and propellant storage. Both, however, possess an instability characteristic which gets them into trouble in the compatibility sense. This characteristic consists of slight dissociation into perchloric acid and base.

(U) Samples of DOAP supplied to the program were inferior in quality. The data are thus suspect, but indicate an inherent thermal stability inferior to that of HAP.

## **The Energetic NF Plasticizers**

(C) TVOPA and P-722 are the best of the group and in our estimation they measure up quite well at ambient and at substantially elevated temperatures. Further, neither TVOPA nor P-722 gives evidence of incipient instability.

(C) P-BEP stability is not simply described. The as-produced product has been variable in composition and in thermal stability, and contains fractions of differing stabilities. Numerous post-manufacturing treatments have been studied, with real but variable improvements. At ambient temperatures state-of-the-art P-BEP is prone to HF elimination reactions and to complications which result therefrom. This phenomenon is more extensive at modestly elevated temperatures. The significance of this observation lies more in the nature of the phenomenon than in its magnitude. HF elimination can be the source of much difficulty; a real propellant, though, may have a built-in mechanism for minimizing or eliminating the generation of HF and/or its undesirable side effects. Nevertheless, from our experience state-of-the-art P-BEP must be classified as incipiently unstable, unstable in a manner which poses a threat to the whole propellant.

## **Aluminum Hydride**

(C) The stability of  $\text{AlH}_3$  has been much studied; contributions from this program to the stability picture have been relatively minor, at least in the volume sense. We concur with the general opinion that  $\text{AlH}_3$  is dangerously close to being too unstable for propellant use. We also subscribe to the belief that cause for the instability ( $\text{H}_2$  evolution) of  $\text{AlH}_3$  is still an unknown, and is susceptible to improvement and/or control. This

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latter statement by no means demeans the substantial effort already expended on AlH<sub>3</sub>.

### **B. Compatibility**

(U) The compatibility of a propellant ingredient differs as the second substance varies, and a simple statement of compatibility is not usually possible.

(C) HP-2 did not appear to be a vigorous oxidizer when combined with binder prepolymers. HP-2 has, however, one property which generally is a serious handicap--it dissociates too readily, and in effect offers perchloric acid to its environment. The environment usually responds to the strong acid rather than through oxidation. Acid promoted cleavage, dehydration and rearrangement of binders are common effects; the latent oxidizing power of perchloric acid is exhibited either as a secondary effect or at elevated temperatures. HP-2 was clearly incompatible with P-BEP.

(U) One of the most interesting observations of the program came from mass spectrometric examination of a whole propellant based on HP-2. The mass spectra revealed storage instability traceable without question to HP-2.

(C) HAP is somewhat like HP-2 in that it is the salt of perchloric acid and a moderately strong base. Dissociation into perchloric acid and hydroxylamine occurs less readily than does the first dissociation of HP-2. Acid promoted chemistry thus occurs less readily with HAP than with HP-2. Such reactions do occur, however, and very probably are the reason for frustrating experiences in formulation of HAP based propellants. Most of the compatibility data obtained with HAP show the oxidizer to be unreactive in the oxidative sense.

(C) TVOPA and P-722 measure up to compatibility requirements with little necessity for qualification although neither is completely inert, of course. We did not see evidence of reactivity, at ambient to above 60°C, sufficient to cause concern that TVOPA and P-722 would interfere with cure chemistry or store poorly in a finished propellant.

(C) With most substances, P-BEP appeared to be more reactive or unstable than it is by itself. However, the combination AP with P-BEP appeared to be slightly more stable than P-BEP alone. The most interesting combination is P-BEP-AlH<sub>3</sub>: The amount of volatile products of decomposition from this combination are less than from either material by itself. The natural conclusion, that the two stabilize one another, has much potential.

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significance. First, P-BEP and AlH<sub>3</sub> are desirable co-ingredients in an advanced propellant; the observation and conclusion justify optimism about prospects for such a propellant. This optimism is raised even further by the results of scavenger studies undertaken during the final phase of this program. Secondly, the (apparent) observed phenomenon portends stabilization of P-BEP and AlH<sub>3</sub>, separately or in combination, by techniques founded on a solid rationale.

(C) P-BEP is relatively incompatible with HAP. This fact is discouraging in that HAP-AlH<sub>3</sub>-P-BEP would be a high performance propellant. One might expect the apparent marginal stability of P-BEP to be paralleled by a relatively high degree of reactivity. As mentioned above, HAP and HP-2 are reactive with P-BEP; enhancement of reaction or decomposition is definite though not great.

(C) The compatibility characteristics of AlH<sub>3</sub> have for the most part been covered above. Any statement about compatibility must be qualified; "AlH<sub>3</sub>" has been treated several ways to modify and improve stability, chiefly to reduce the rate of hydrogen evolution. We looked at the compatibility of only one lot of AlH<sub>3</sub>. AlH<sub>3</sub> generally appeared to be unreactive and the amount of hydrogen evolved from two component AlH<sub>3</sub> systems is about the same as it is from AlH<sub>3</sub> alone. Our studies were set up to obtain average data over relatively long periods of time, however, and we probably would have missed short term (possibly cyclic) differences attributable to surface properties.

(U) Hydrogen fluoride reacts readily with AlH<sub>3</sub>, yielding hydrogen and Al-F species. This fact discourages use of AlH<sub>3</sub> in a system containing potential HF generators, i.e., P-BEP, and would seem to be inconsistent with the enhanced stability (lessened gas evolution, including hydrogen) of P-BEP-AlH<sub>3</sub> mixtures. This question requires further study.

(U) Noteworthy is the fact that a variety of volatiles are evolved when AlH<sub>3</sub> is contacted with large amounts of HF; carbon monoxide, carbon dioxide, nitrogen and silicon tetrafluoride are among the products, in more than trace quantities. Silane was observed in other studies of AlH<sub>3</sub>. While no one claims ultra purity for AlH<sub>3</sub>, it is easy to forget that impurities are present and thus neglect to consider their effects. The volatiles generated by HF serve as a reminder of the purity problem, and studies of the origin of substances such as carbon monoxide could help to better characterize AlH<sub>3</sub>.

### C. Gaseous Degradation Products

(U) The nature of gases generated by propellant ingredients and ingredient combinations deserves mention. Certain gases are consistently present over nearly all ingredients and ingredient combinations. If the proper elements

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are present in the system, one can confidently expect to see N<sub>2</sub>, N<sub>2</sub>O, and CO<sub>2</sub> after an appropriate time at a specific temperature. Carbon monoxide and nitric oxide are nearly as prevalent as the above gases. One would expect to see water routinely, but water apparently absorbs strongly and is observed only under conditions of high vacuum, as in the mass spectrometer.

(U) Nitrogen is an inert gas and is objectionable in a cured propellant. Carbon monoxide, nitric oxide and nitrous oxide are more reactive, but they are sufficiently inert to be a problem and a source of physical changes in a propellant. Also the above oxides can react in a propellant grain, inflicting unwanted alterations in propellant properties.

(U) Methane is observed quite frequently, even in systems which contain oxidizers. Methane must be viewed as a refractory, and its presence is both somewhat inexplicable and objectionable. We offer no mechanism for its formation. It is apparent, however, that methane is a stable by- or end-product of complex reactions variously involving cleavage, rearrangement, dehydration, and oxidation of organic constituents.

(U) Several simple organic molecules, such as ethylene, methyl formate, methyl ether, ethyl ether, and organic esters appear occasionally. These substances are likely not generated in harmful quantities; they are, however, symptomatic of changes within the binder framework which may adversely and significantly alter physical properties.

(C) P-BEP yields most of the usual products (NO, N<sub>2</sub>, N<sub>2</sub>O, CO, CO<sub>2</sub>) along with substances unique to a C-N-F material. HNF<sub>2</sub>, NF<sub>3</sub>, HCN, and HF have been observed. HF and HCN are primary and major products of decomposition. Difluoramine and nitrogen trifluoride are minor products.

### **D. Assessment of Advanced Ingredients**

(U) One substance, ammonium perchlorate, has consistently performed well in current propellant systems. AP has been in use for some time, is a respected substance in the propellant application sense, and this program has not uncovered novel information to contradict that claim. Experience on the program emphasizes the point that AP is deserving of respect; the frailties of the newer materials become obvious when compared with AP. This general observation is the basis for sober reflection, to wit: AP, with very few inherent and obvious weaknesses, did not submit meekly to its role in propellantry, and is still not the universal answer; we should thus expect a considerable challenge from substances with obvious weaknesses.

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(U) The propellant industry should, in the development of advanced ingredients, keep in mind the fact that AP became a tractable and valuable oxidizer only after a few important rules regarding its use were spelled out. The "rules" for advanced ingredients are not yet adequately defined. The issue at hand is simple: What are the prospects for finding the rules? And are weaknesses in an ingredient sufficiently significant to justify elimination of the ingredient from consideration?

(U) From the vantage point of this program, our current answers to these questions are as follows.

(C) HP-2 has a basic weakness which justifies shelving it for the present. The weakness manifests itself readily in the laboratory, and development activities have been frustrated by the effects of the weakness. Further efforts, if any are deemed desirable, should concentrate on a fundamental approach to mitigation of the effects of the acidic character of HP-2.

(C) HAP's basic flaw derives from the fact that it is not quite strong enough a union of a strong oxidizing acid and an inherently unstable base. "Not quite," and "almost" seem to have become typical HAP descriptors, and there is a strong tendency to feel that success must be just around the corner because it really behaves pretty well. We have come to the conclusion that the facts now say to the industry that any further effort should directly address the basic weakness of HAP--in a laboratory based search for means, to make the oxidizer more stable and compatible.

(C) TVOPA and P-722 are, on the basis of the laboratory studies, substances suitable for continuing development. Further activities hinge more on finding suitable systems for their use, than on the questions of stability and compatibility.

(C) P-BEP is structurally similar to TVOPA and P-722 both of which appear to be propellant-trustable materials. However the current manufacturing process for P-BEP yields a "mixture" whose constituents vary in stability and reactivity. The "mixture" consists of a range of molecular weights as well as some degradation products. The properties of P-BEP are in principle amenable to control and to improvement through process modification or through post-manufacturing treatments. Progress is being made in these areas, and in the fundamental sense P-BEP can be improved to the point of being comparable to TVOPA. Results of efforts to develop stabilizing additives for P-BEP, such as hexamethylborazine, are encouraging.

(C) Current results indicate the P-BEP and AlH<sub>3</sub> help one another in a stability-compatibility sense. One concludes that "P-BEP" is suffering (for the most part) from man-made rather than inherent flaws, that progress in control and improvement is encouraging and real, and that these factors

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in combination with the potential worth of a P-BEP-containing system justify continuing research and development.

(C) The overriding concern with AlH<sub>3</sub> is hydrogen evolution. Hydrogen has been generally attributed to the instability of AlH<sub>3</sub>, rather than to reaction with the environment. Studies conducted at Midwest Research Institute under this program are a relatively minor part of the total effort, and we thus, must base an analysis on limited internal experience and on knowledge of activities elsewhere. We tend to be much encouraged by the observation that AlH<sub>3</sub> is (apparently) more stable in a real, useful system than it is by itself. We have generally found AlH<sub>3</sub> to be more stable (less H<sub>2</sub> evolution) after some months than indicated by the supplier. Our program yielded evidence indicative of stabilization by thermal soaking--this bit of evidence takes its place alongside a multitude of reports and observations that the stability of AlH<sub>3</sub> has been altered and improving by treatments of various sorts. We have become convinced, as a consequence of working with AlH<sub>3</sub> and hearing of the experiences of others, that "stability of AlH<sub>3</sub>" is: (1) not constant with time; (2) likely more a function of the surface than of the interior of a particle, and therefore, is in a sense a compatibility problem; (3) in need of control by chemical-physical means (surface property control) in a propellant--that pretreatment before introduction into the propellant may yield only a temporary improvement; and (4) is probably considerably better than it is credited with being; this conclusion is based on the belief that instability is predominantly of surface origin. In summary, we think that AlH<sub>3</sub> can be used in propellants, but that the job will require perseverance and time.

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IV.

## EXPERIMENTAL PROCEDURE

The experimental procedures used routinely through the program were infrared spectroscopy, gas chromatography, and mass spectrometry. The basic problem in a program of this type is one of designing the experiments in such a manner that as much useful information as possible can be generated as simply as possible. In this program, such information could be found by analyzing the gaseous products generated during the experiment. It was found, for example, that simple products ( $\text{CO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{CO}$ ,  $\text{H}_2$ , etc.) were evolved in significant amounts from the binder-oxidizer systems, despite the fact that changes in the condensed system could not be accurately measured. The use of gas phase analysis also permitted us to analyze a large number of samples routinely, to study a large number of ingredient combinations under a variety of conditions, to pinpoint potential problems which would occur in propellant formulation at an early stage, and thus recommend remedial action before the particular problem became major.

This discussion will be divided into the following sections: sample preparation, analysis of evolved gases by infrared, analysis by gas chromatography, analysis by mass spectrometry, and analysis of the condensed phase.

### A. Sample Preparation

The systems which did not contain fluorine were placed in glass break-seal tubes, evacuated, allowed to stand at constant temperature for a specific time, and finally opened so that products evolved in the gas phase could be analyzed. The systems containing fluorine were subjected to the same conditions, except that the samples were prepared in 1/4-in. passivated stainless steel tubing.

The glass break-seal tubes used were made in the laboratory (Figure IV-1). These tubes consisted of a U-tube (AB) with one end sealed off. A piece of glass (BC) was joined to the seal at B to provide a path for sampling the gases for analysis. The sample was introduced into the break-seal through Section A. The Section AB was then evacuated and sealed at Point D. The sample was then placed in a constant temperature bath until it was analyzed.

At the time of analysis, a nail was carefully placed into Section BC of the break-seal tube. The tube was attached to a 10-cm. infrared cell at C, and the cell plus Section BC of the break-seal tube were evacuated.

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10/30 GROUND GLASS FITTINGS

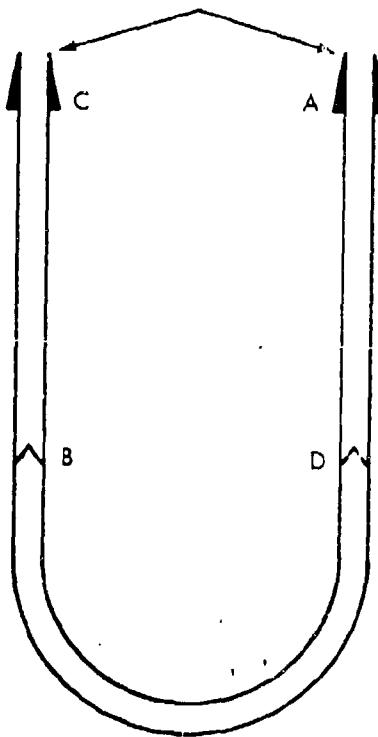


Figure IV-1 - Glass Break-Seal Tube

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The nail was then raised above the break-seal with a magnet, and released to puncture the seal at Point B. The evolved gases then filled the cell and could be analyzed.

The infrared spectrum of the gases was taken first. The cell was then attached to a gas sampling valve on a gas chromatograph, and the gases analyzed by that technique.

In the case of fluorine-containing systems, glass was an unsatisfactory container for the materials, since the fluorine species attacked the glass, forming large quantities of silicon tetrafluoride,  $\text{SiF}_4$ . Therefore, it was necessary to study these systems in metal tubes as shown in Figure IV-2. A 6-in. stainless steel tube was used as the body. One end was capped and the other attached to the brass valve. The sample was placed in the stainless steel cap at the base and screwed on to the tube. A connecting joint on the open end of the valve permitted the tube to be evacuated. After evacuation, the sample was stored for subsequent analysis at the proper time.

The infrared cell used with the metal tubes was constructed of Kel-F tubing. This material was necessary to prevent the reaction of highly reactive fluorine species (HF and  $\text{HNF}_2$ ) with the glass contained in an ordinary cell. The gases were analyzed using infrared and gas chromatography.

Throughout the program, about 100 mg. of material was evaluated in each sample. This small quantity of the sample, and the fact that the volume into which gases were liberated varied slightly from sample to sample, are the chief apparent sources of experimental error. The analyses by infrared and gas chromatography involved comparison of peak height to working curves constructed from analyses of standard samples of gases at known pressures and volumes.

## B. Analysis of Gaseous Species by Infrared

As described above, the tubes which contained the materials for compatibility studies were opened into 10-cm. infrared cells. The evolved gases were then analyzed using a Beckman IR-12 spectrophotometer. The infrared technique was used to determine HF, HCN,  $\text{HNF}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{SiF}_4$ ,  $\text{CH}_4$ , and various esters, ethers, and fluorocarbons which were evolved during standing. In the case of  $\text{AlH}_3$  studies, we also detected  $\text{SiH}_4$ ,  $\text{HCl}$ , and fluorosilanes.

The sensitivity of the IR technique is dependent upon the species being investigated. The minimum sensitivity for HF is only about 1 mm. pressure, while the minimum sensitivity for  $\text{SiF}_4$  is 0.01 mm. Therefore, there

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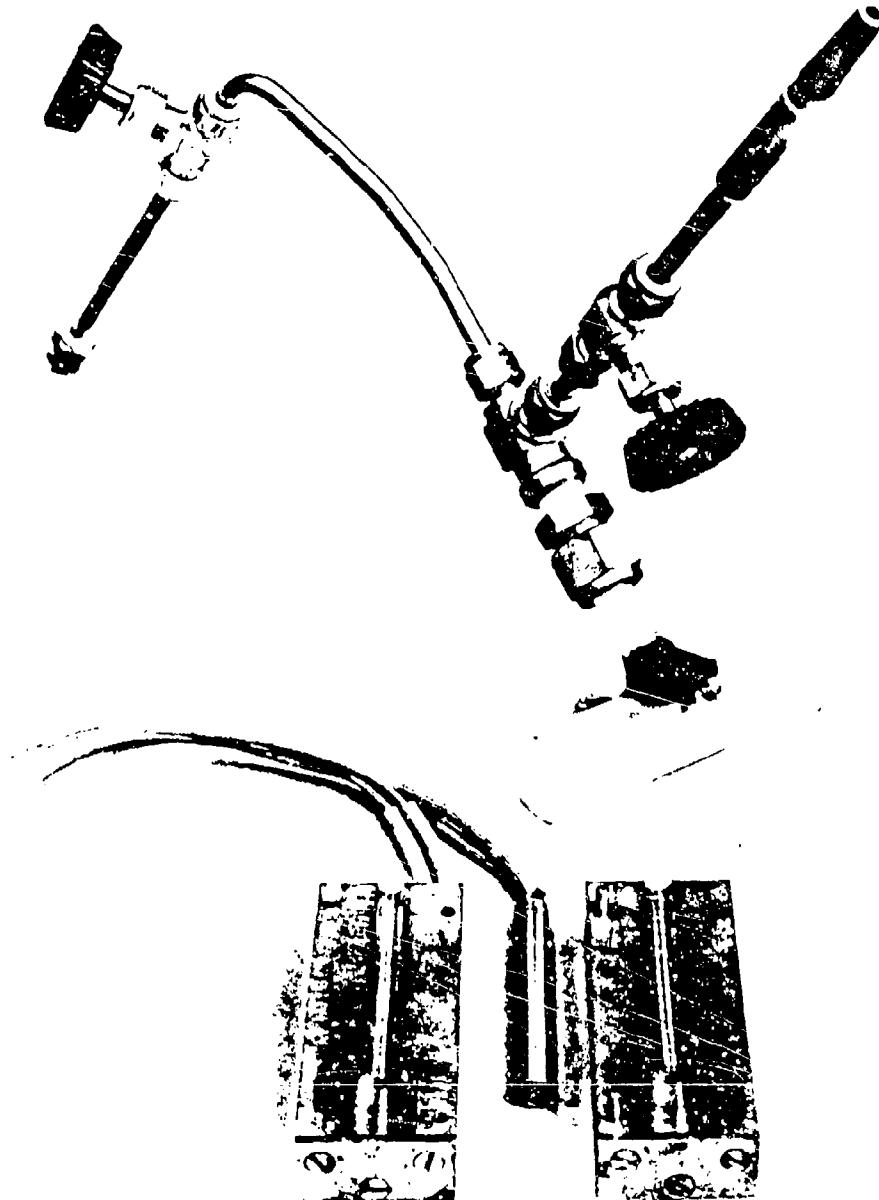


Figure IV-2 - Thermocouple-Controlled Brass Block Heater Metal Sample Holder and Kel-F Infrared Cell

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is always the suspicion that traces of other products are undetected due to their low sensitivity. However, when the IR technique is backed up by others, gas chromatography and mass spectrometry in this case, these doubts are diminished.

Fortunately, gaseous species not detected by IR could be readily detected by GC. In the case of N<sub>2</sub>O, both IR and GC can be used and serve as cross checks on one another. In those samples which contained N<sub>2</sub>O, the results obtained using these techniques agreed reasonably well.

The data obtained were reported in milliliters of standard gas per gram of sample. As mentioned earlier, the principal uncertainties are the variance in sample volume (hence, expanded volume) and the variance in weighing 100 mg. of sample. However, results with multiple samples held under the same conditions indicated that the general procedure gave data sufficiently accurate for our purposes.

### C. Analysis of Gaseous Species by Gas Chromatography

Following analysis by infrared, the samples were subjected to a gas chromatography. The infrared cell was attached to a gas inlet valve on a Perkin-Elmer Model 154 gas chromatograph. The inlet valve was evacuated before the gas sample was introduced. The gases were then separated on a Porpak Q column. The detectors were a set of balanced thermistors which measured differences in heat conductivity of the sample gas and the helium carrier gas.

The column was cooled to about -15°C during the run. The cooling permitted the separation of N<sub>2</sub>, O<sub>2</sub>, CO, and NO which fall practically on top of one another if the column is at room temperature. In addition to the above mentioned gases, H<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub>, and N<sub>2</sub>O were also determined.

The identification of gas was accomplished by residence time between injection and detection, and the amount of gas by the peak height of the recorder trace. Each sample was analyzed twice (two injections).

The GC technique provided the most accurate analytical data of the compatibility studies. However, its major limitation is the number of species which could be detected. Again, these data were related back to milliliters of gas evolved per gram of sample, and the inherent sources of error discussed earlier apply here also.

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D. Analysis by Mass Spectrometry

One of the unique series of experiments conducted in the study was the analysis by direct inlet mass spectrometry. Here, small quantities of sample were placed directly into the mass spectrometer, heated, and the evolved gases analyzed. Thermal degradation was studied as a function of time at constant temperature or at a programmed heating rate. This technique could perhaps be defined as a sophisticated DTA or TGA experiment coupled with a gas analysis system. However, it affords much higher inherent sensitivity to degradation than does either DTA or TGA. Through the use of a dedicated computer for accumulating, storing and processing data, the utility of this instrument has been increased at least an order of magnitude.

E. Condensed Phase Studies

Analyses of condensed phases (the material from which gases were evolved) were for the most part disappointing. Despite the fact that significant quantities of gas were evolved, no significant change in the composition of the residue could usually be detected by conventional techniques. The techniques used were infrared, nuclear magnetic resonance, and electron spin resonance spectroscopies.

Electron spin resonances indicated that some change did occur in a real propellant after standing for prolonged periods. When the sample was investigated in the ESR spectrometer, a fairly strong peak was detected in the  $g = 2.0$  region indicating the presence of free radicals in the solids. The peak was a broad singlet and could not be characterized. Upon standing, the intensity of this peak increased, indicating perhaps that further degradation had occurred. Unfortunately, the past history of the sample prior to receipt was unknown, so that the changes observed could not be related to specific events.

Several residues were examined specifically, expecting to see some changes in the ESR analysis. Despite the fact that these residues appeared to be charred, no meaningful results were obtained.

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V.

OXIDIZER STUDIES

(C) A large portion of the early effort on this program was devoted to studies of the stability of hydroxylammonium perchlorate (HAP) and hydrazinium diperchlorate (HP-2) and to their compatibility with binders and curing agents. Binders investigated included hydroxy- and carboxy-terminated polybutadiene and polyisobutylene prepolymers, and poly[1,2-bis(difluoramino)-2,3-propylene oxide] (P-BEP). Compatibility studies with P-BEP are described in Section VI. The curing agents studied included isocyanates, aziridines, and epoxides. Studies with AP were included to provide a baseline for comparing the relative compatibility of the two more energetic oxidizers.

(C) Later in the program, and after HP-2 was essentially eliminated as a candidate oxidizer, compatibility of HAP with two NF plasticizers, 1,2,3-tris[1,2-bis(difluoramino)ethoxy] propane (TVOPA) and 2,3-bis(difluoramino)-propyl-2,2-dinitropropylcarbonate (P-722) and with aluminum hydride (LMH-1) were studied, Sections VII and VIII, respectively.

(C) Some preliminary studies were also conducted on the stability and compatibility of the RPL developed oxidizer, methylene dioxyamine diperchlorate (DOAP).

(C) At the time this program was initiated, nitronium perchlorate was being eliminated as a candidate advanced oxidizer, HAP and HP-2 were still considered to be attractive oxidizers and DOAP was still in the minds of its synthesizers. It should also be recalled that at that time many of the difficulties with HAP and HP-2 were similar to those encountered in early attempts to formulate stable propellants with AP.

(C) During 1967, it became increasingly apparent that HP-2 afforded little prospect of being used in an advanced propellant system, particularly in conjunction with NF binders, plasticizers, and the advanced fuels. HAP, which was slightly more attractive from a compatibility viewpoint than HP-2, was carried along as a candidate advanced oxidizer. In 1968, DOAP appeared to be an attractive advanced oxidizer candidate and is still a subject of interest to the Air Force.

(C) At the completion of this program, HAP and HP-2 cannot be considered attractive candidates for use in advanced propellant systems.

(U) This section of the report covers studies conducted on oxidizer stability and on oxidizer compatibility with binder prepolymers (excluding P-BEP), curing agents and some whole propellant studies.

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## **A. Background**

(C) A number of studies have been conducted on the thermal stability of HAP, with the decomposition products commonly observed being N<sub>2</sub>O, H<sub>2</sub>O, and NO (Ref. 1). It was reported that no decomposition occurred below the melting point of HAP (~ 86°C) and the decomposition scheme became very complex above 160°C. The Elkton Division of Thiokol reports little or no decomposition below 160°C (Ref. 2). The Reaction Motors Division of Thiokol reported that HAP decomposes autocatalytically at 130°C (Refs. 3 and 4) by two processes. Activation energies of 37 kcal and 63.2 kcal were reported for the two decomposition schemes which occur in the temperature region 130°C to 160°C. DTA studies on HAP show a small endotherm at about 60°C. This endotherm has been attributed to both a crystal phase transition (Ref. 5) and to dehydration (Ref. 6).

(U) The stability of hydrazine diperchlorate (HP-2) has also been studied extensively. Again, there is a fair amount of discrepancy in the literature as to where decomposition of HP-2 begins to occur. Little decomposition was observed in 35 days at 140°C (Ref. 3). Grelecki and Cruice (Ref. 7) reported that the decomposition of HP-2 is autocatalytic; at 120°C the reaction showed a sharp transition to rapid decomposition after 77 hr. No indication of the minimum temperature for decomposition was reported. It was reported that anhydrous perchloric acid and perchloric acid dihydrate both accelerate the decomposition of HP-2. Hydrazine monoperchlorate (HP-1) is a primary decomposition product of HP-2 and appears to be slightly more stable than HP-2. The decomposition of perchloric acid was suggested as the controlling step in the decomposition of both HP-1 and HP-2.

(U) Ammonium perchlorate (AP) is substantially more stable than HAP and HP-2. This oxidizer exhibits an endotherm at 245°C and is generally agreed to show little or no decomposition below this temperature. Maycock et al. (Ref. 8 and 9) have conducted a mass spectrometric investigation of the decomposition of AP at 230°C. From the data, they calculate  $\Delta E = 17$  kcal/mole for O<sub>2</sub> and Cl<sub>2</sub>.

(U) The compatibility of HAP, HP-2 and AP with a number of propellant ingredients has been investigated. Studies previously conducted at MRI (Ref. 10) have shown that neither HAP nor AP promoted extensive oxidative degradation of binder prepolymers. Instead, reactions such as: rearrangement of ethers, dehydration of alkoxyl and ethers, polymerizations of epoxides and olefins were found to be much more common and important. These results have been substantiated in more recent studies (Refs. 11 and 12).

(C) In all cases both HAP and HP-2 were found to be considerably more reactive than AP with other propellant ingredients.

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## B. Experimental

1. Material handling: HAP used in this study was obtained from the Elkton Division of Thiokol Chemical Company. This oxidizer was 97% pure based on a titration for weak acid. The material was not subjected to further purification before use.

HP-2 was obtained from the Wasatch Division of Thiokol Chemical Company. Two different samples were furnished. The analyses of both lots were very similar: 97.8% HP-2, 0.3% AP, 0.1%  $\text{HClO}_4$ , and 0.8% unknown.

DOAP was supplied by the Air Force Rocket Propulsion Laboratory. It was found to be 80-85% pure by perchlorate analysis and titration of strong acid. A weight loss of 13-14% occurred when the material was evacuated 16 hr. at  $10^{-5}$  torr. The evacuated sample was 93-95% pure by titration. DOAP treated by this method was used for the stability and compatibility studies.

AP was obtained from G. Frederick Smith Chemical Company. The storage and handling of all these oxidizers were performed in a dry box having a -80°F dew point.

Binder prepolymers studied on this program include: hydroxyl terminated polyisobutylene (UTREZ-diol), and carboxyl terminated UTREZ; hydroxyl terminated polybutadiene (R-45-M), carboxyl terminated polybutadiene (Telagen CT); saturated hydroxyl terminated Telagen; a carboxyl terminated polyisobutylene (EMD-590); and two ethyl acrylate-acrylic acid copolymers. These prepolymers were selected on the basis of recommendations of propellant formulators.

Curing agents investigated included: isocyanates (DDI, TDI, HMDI, PAPI, and CTI), an epoxy (ERLA-4221); and an aziridine (MAPS).

All binder prepolymers and curing agents were used as received after being stripped of solvent and were handled in the dry box.

2. Experimental procedures: The relatively low temperatures employed in these studies required the use of sensitive analytical techniques to detect and identify the decomposition and reaction products being generated. No single experimental technique is presently available which would yield all of the information needed to identify the types and quantities of gaseous products evolved, and chemical changes in the residue. As a consequence IR and NMR spectroscopy, gas chromatography and mass spectrometry were employed in the studies. The special advantages of each technique (sensitivity, identification, quantitative analysis, etc.) were exploited and the results integrated to give a comprehensive picture of the types of reactions occurring.

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(U) The majority of the reactions were quite slow under conditions used in these studies. Since time periods of several weeks were necessary to detect a significant amount of reaction in most instances, the reactants were placed in evacuated ( $10^{-5}$  torr) glass break-seal tubes, immersed in constant temperature baths, and removed for analysis after standing for weeks or months. The temperatures used in these studies were 25, 40, 55, and 70°C. These temperatures were selected to correspond to curing temperatures employed in propellant formulation and propellant storage. The quantities of oxidizer varied from 50 to 150 mg., and the quantities of other reactants were approximately 100 mg.

(U) The thermal stability of a number of the materials was also investigated by direct inlet mass spectrometry. This technique consists of placing milligram quantities of a material in a gold crucible which is inserted directly into the mass spectrometer to a distance of 1 mm. from the ion source. The temperature of the crucible is externally controlled. The temperature is increased as desired and mass spectra of the evolved gases recorded. The technique is extremely sensitive and capable of detecting and identifying trace quantities of decomposition products.

### **C. Oxidizer Stability**

(U) Oxidizer stability was studied by analyzing for gaseous decomposition products. IR spectroscopy, gas chromatography, and mass spectrometry were utilized in these studies.

(U) 1. Long-term thermal stability: Samples of as-received HAP and HP-2 were placed in evacuated glass break-seal tubes immersed in the 70° bath and allowed to stand for 35 and 72 days. Nitrogen is the most common gaseous decomposition product observed from HP-2, while N<sub>2</sub>O is commonly a decomposition product of HAP (Ref. 10). Water is not detected in the gas phase since it is strongly absorbed by the oxidizer. No gaseous decomposition products were detected by IR, GC or mass spectrometry from either HAP or HP-2 after 36 days at 70°C. After 72 days at 70°C traces of NO and N<sub>2</sub>O were detected from HP-2.

(C) The as-received DOAP was analyzed by titrating with sodium hydroxide and for total chlorine. Only the first acid group could be determined by titration. Two samples tested had a purity of 85.6 and 86.0% of theoretical. Perchlorate analysis of the as-received DOAP gave 81.7 and 82.7% of theoretical chlorine.

(C) A sample of as-received DOAP which was dried in a 55°C oven for 1 hr. liquefied and did not recrystallize when cooled to room temperature although some crystalline material was present. A 13-14% weight loss was observed

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when a second sample was evacuated at  $10^{-5}$  torr for approximately 16 hr. The principal constituent lost during evacuation was nitromethane, the solvent used during synthesis. Titration of the evacuated sample for acid showed a purity of 95.4% while total chlorine analysis gave 93.3%.

(C) A sample of the vacuum-dried DOAP liquefied in the dry box after standing at ambient temperature for 2 weeks. The DOAP which liquefied in the oven gave two sharp endpoints when titrated with base. The two acids titrated were of approximately equal concentration. Total titratable acid was about equal to the acid normally found by titration. Total chlorine analysis of this liquid gave 96.3% of theoretical.

(C) Investigators at AFRPL (Ref. 13) have proposed a stepwise decomposition mechanism for DOAP in which the initial step involves loss of one perchloric acid group at about 60°C. As the temperature increases the remaining monoperchlorate salt undergoes a concerted cleavage rearrangement to give formamide and hydroxylammonium perchlorate. The latter can further decompose to form ammonium perchlorate among other species.

(C) The liquid phase of the decomposed DOAP can consist, according to this scheme, of a solution of HAP and  $\text{HClO}_4$  in formamide, and the crystalline material being AP. The strong acid titrated is apparently  $\text{HClO}_4$  which may be partially associated with formamide while the weak acid is HAP. These two acids are present in approximately equal molar concentrations, which fits the decomposition scheme. A NMR of the liquid shows the presence of  $\text{CH}_2$  groups which are likely due to residual DOAP.

(C) The thermal stability of DOAP was studied at 25, 40, 60 and 80°C. While both HAP and HP-2 showed only trace amounts of gaseous decomposition products after 72 days at 70°C, DOAP liberated 2-3 ml. of gas per gram at 60°C in 32 days and 15-20 ml. at 60°C in 90 days. The gaseous product consisted mainly of CO and lesser amounts of  $\text{N}_2$ ,  $\text{CO}_2$ , and  $\text{N}_2\text{O}$ . The data obtained on these studies are shown in Table V-I.

(U) 2. Direct inlet mass spectrometry: Mass spectrometric studies, using an Atlas Model CH-4B instrument, were conducted on HP-2 and HAP. The direct inlet technique used in these studies has been described previously (Ref. 14). All samples were prepared in a dry box with a dew point of -80°F and maintained under an inert atmosphere until the sample was degassed at the ambient temperature in the mass spectrometer. After degassing, the temperature of the sample was normally raised in 10°C increments. At each temperature, one mass spectrum was obtained as soon as the temperature had equilibrated and another after the sample had remained at constant temperature for 4 to 5 min. The nominal ionizing voltage in all of these studies was 70 ev.

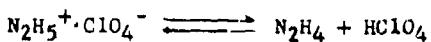
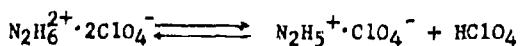
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TABLE V-I

GASEOUS PRODUCTS FROM NEAT DOAP (LOT E-13)  
(Ml. of gas/g of DOAP)

Time (days)	Temperature	N <sub>2</sub>	CO	CO <sub>2</sub>	N <sub>2</sub> O	Other
32	25	-	-	-	-	-
	40	-	tr	-	-	-
	60	0.2	2.1	0.2	tr	HCl (tr)
	80	tr	15.5	1.5	2.9	HCl
32	25	-	-	-	-	-
	40	0.1	tr	-	-	-
	60	0.3	2.3	0.1	0.8	HCl (tr)
	80	0.1	9.2	0.8	1.6	HCl
90	25	-	tr	-	-	-
	40	-	0.2	-	-	-
	60	0.8	18.8	1.5	1.8	HCl (tr)
	80	0.5	27.5	3.1	0.3	HCl (tr)
90	25	-	tr	-	-	-
	40	-	0.4	-	-	-
	60	0.7	14.5	1.1	1.8	HCl (tr)
	80	0.8	25.9	2.5	3.1	HCl (tr)

(U) a. HP-2: Hydrazinium diperchlorate was studied over the temperature range of 30 to 140°C. The results for two of the ions observed in this study are shown in Figure V-1, with the ClO<sub>2</sub><sup>+</sup> ion being representative of the evolution of perchloric acid. Other ions attributable to the ionization and fragmentation of perchloric acid (m/e 51, 83, 100) were found to provide the same type of intensity vs. temperature curve. These results are in agreement with the earlier observation (Ref. 7) that the principal reactions of HP-2 are a low temperature dissociation into the monoperchlorate and perchloric acid followed by the further dissociation into free hydrazine and perchloric acid at higher temperatures.



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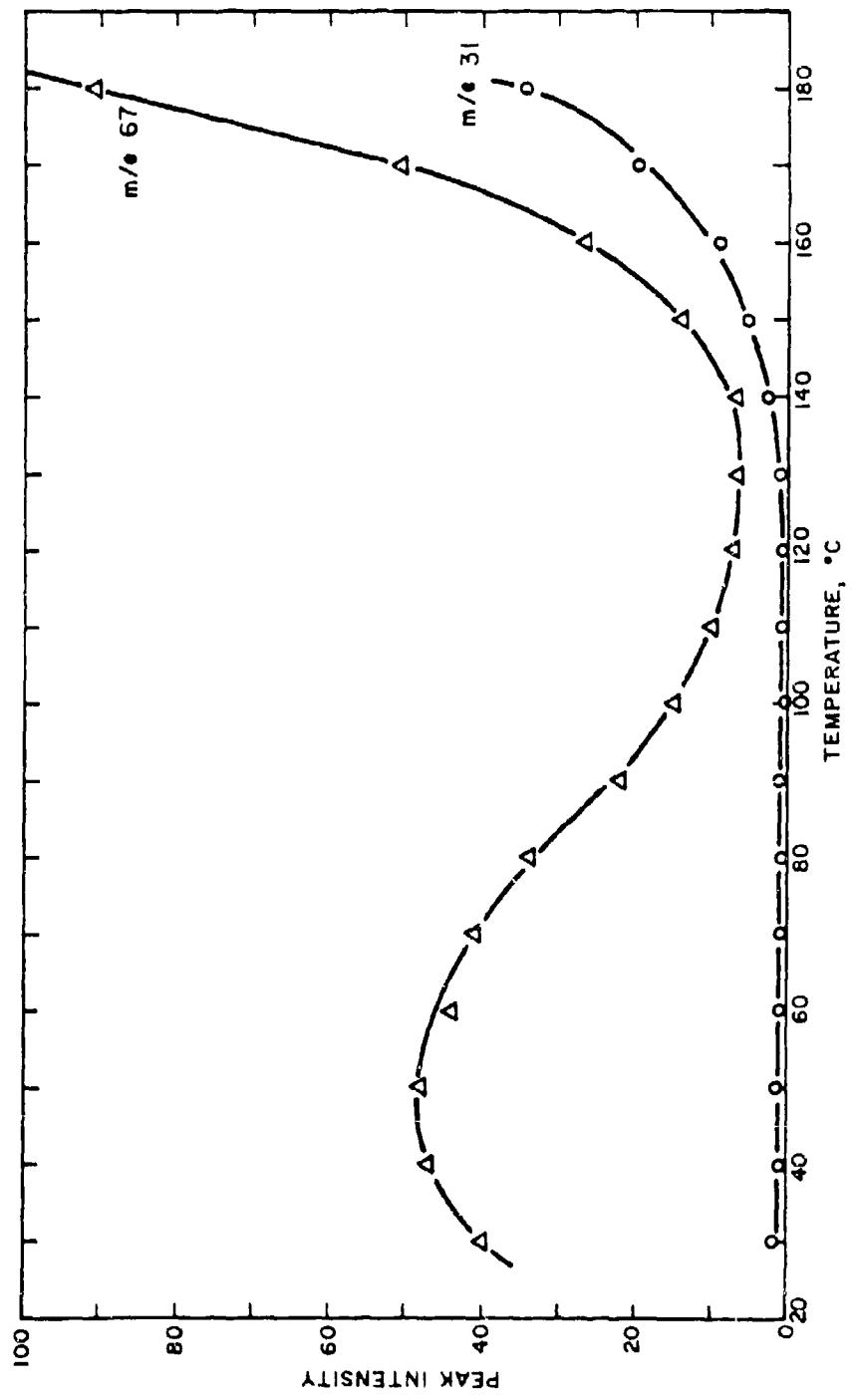


Figure V-1 - Variation of Peak Intensity with Temperature  
for the  $\text{ClO}_2^+$  and  $\text{N}_2\text{H}_3^+$  Ions from HP-2

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The rate of evolution of the first perchloric acid group appears to reach a maximum at approximately 50°C with this particular combination of sample size, pressure, and temperature programming. Above 130°C, the evolution of  $\text{HClO}_4$  from HP-1 proceeds rapidly with temperature up to 180°C, at which point the study was stopped. Free hydrazine formation, as evidenced by the m/e 31 peak ( $\text{N}_2\text{H}_3^+$ ), remained very low up to about 130 to 135°C, whereupon the evolution increased rather rapidly up to 180°C.

A plot of  $\log$  (intensity) as a function of  $1/T$  °K for three of the ions observed in the mass spectra over the temperature range of 140 to 180°C is shown in Figure V-2. The three ions give an average  $E_a = 24.4$  kcal/mole. Grelecki and Cruice (Ref. 7) calculate  $E_a = 23.8$  kcal/mole for HP in the temperature range of 140 to 200°C. Other investigators (Ref. 15) have reported two maxima for perchloric acid evolution from HP-2; the first at  $\sim 84^\circ\text{C}$  and the second at  $\sim 127^\circ\text{C}$ . In addition, they also report a maximum for the  $\text{N}_2\text{H}_3^+$  ion at  $\sim 130^\circ\text{C}$ . For the perchloric acid maximum at  $\sim 127^\circ\text{C}$ , their calculations gave  $E_a = 18$  kcal/mole and for the  $\text{N}_2\text{H}_3^+$  ion,  $E_a = 32$  kcal/mole.

The results of this study have produced insufficient data to calculate an  $E_a$  value for the low temperature evolution of the first perchloric acid molecule. However, the workers from Lockheed (Ref. 14) have shown that a plot of  $\log$  (intensity) vs.  $1/T$  for the first  $\text{HClO}_4^+$  peak, which maximizes at about 84°C, produces a line with a distinct change in slope. The two slopes are termed "lower" and "higher" temperature regions and their calculations show  $E_a = 23$  and 86 kcal/mole, respectively.

b. HAP: A study of the thermal stability of hydroxylammonium perchlorate was attempted using the direct inlet technique. The results of an earlier preliminary investigation showed that the decomposition of HAP proceeded very slowly up to 55°C. Between 55 and 60°C, a sharp increase in the gaseous evolution occurred; however, above 60°C the evolution slowed considerably but maintained a greater rate than that observed below 55°C.

In the course of conducting other studies, this sample of HAP was depleted and a new sample obtained. The results of identical mass spectrometric studies are shown in Figure V-3. It can be seen that the product evolution increases smoothly with increasing temperature and no variation is observed in the 55 to 60°C region. At temperatures above 80°C, gaseous evolution of perchloric acid and hydroxylamine increases very sharply and is most probably due to sublimation and/or vaporization into the ion source.

Due to the difference in the behavior of the two lots of HAP, it cannot be stated, with any degree of certainty, whether or not the

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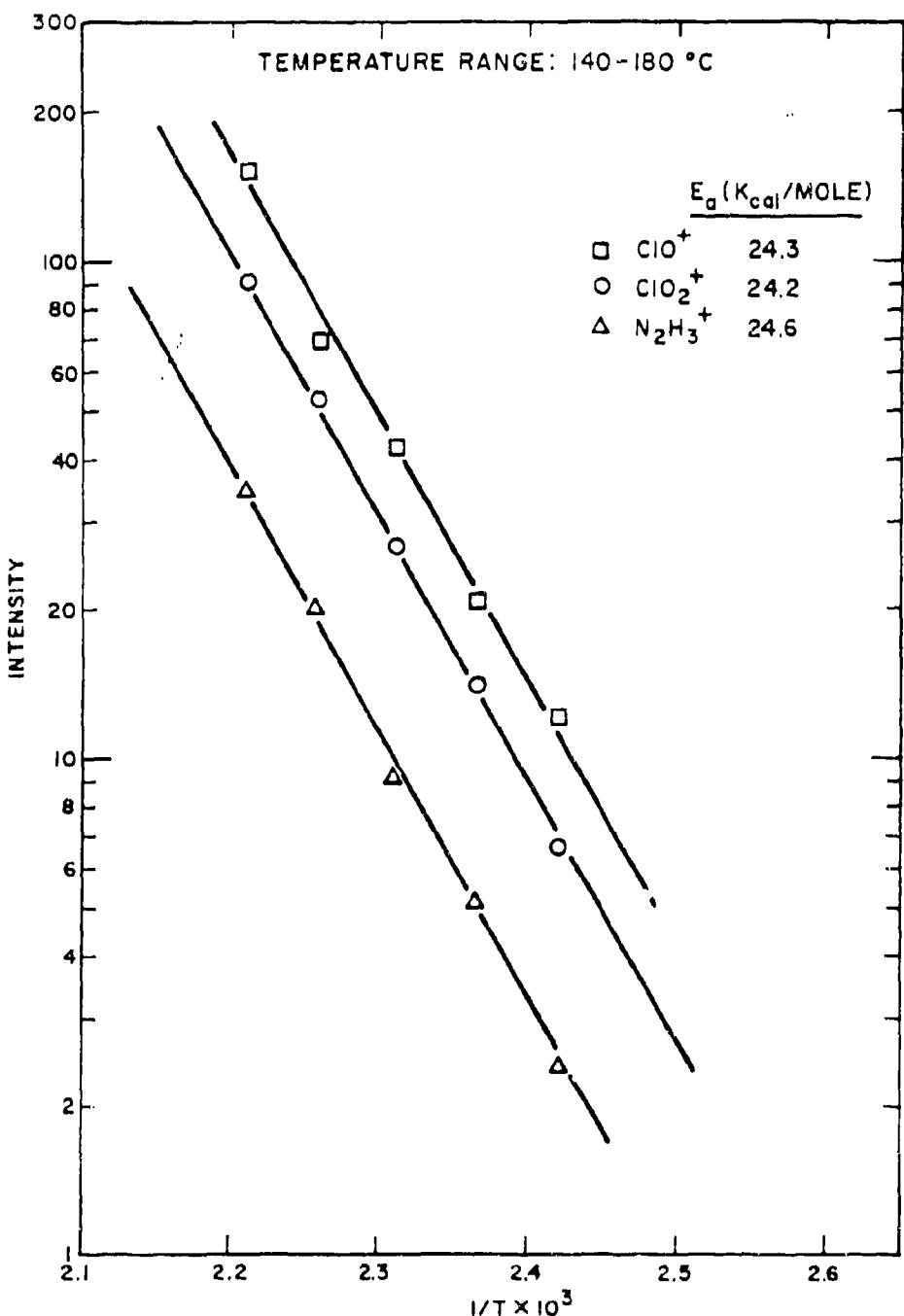


Figure V-2 - Log Peak Intensity vs.  $\frac{1}{T}$  for Three Ions Observed from HP-2

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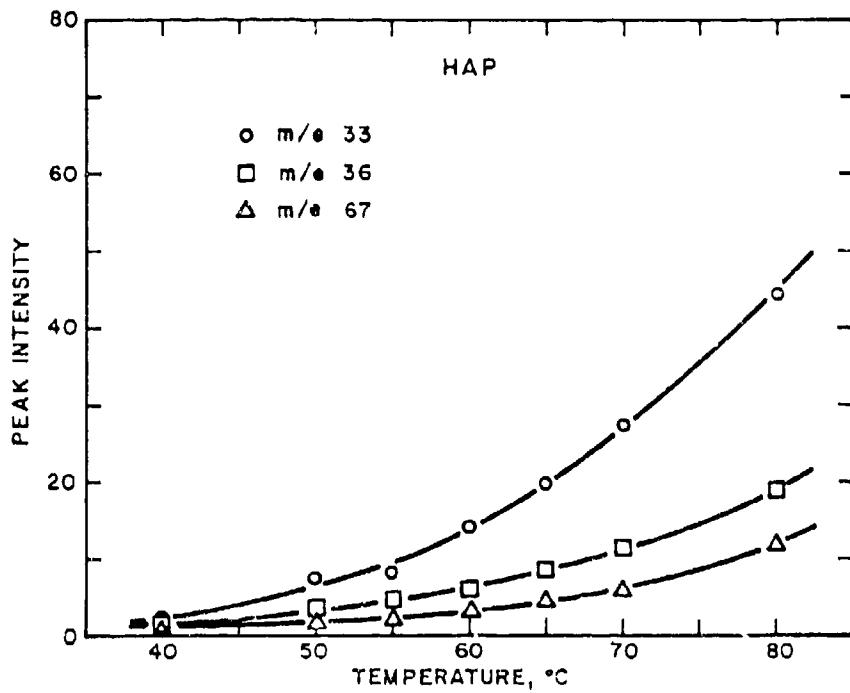


Figure V-3 - Variation of Peak Intensity with Temperature  
for Three Ions from HAP

reported (Ref. 5) crystalline phase change in HAP affects its stability. Moreover, the results can be interpreted as indicating that the reported phase changes are due to the presence of an impurity such as water (Ref. 6).

(C) c. DOAP: Direct inlet mass spectrometer studies on DOAP were not reproducible apparently due to significant lot-to-lot variations as well as within-lot variations. Studies as a function of temperature on as-received material showed many pressure surges as the temperature increased. These pressure surges were attributed to occluded mother-liquor or gas pockets consisting of degradation products. These pressure spikes were not of sufficient duration to obtain a mass spectrum. These pressure surges were partially eliminated by grinding the sample to a fine powder. The principal m/e values observed for DOAP were 28, 30, 44, 45 and 67 and are attributed to CO, N<sub>2</sub>, NO, N<sub>2</sub>O, CO<sub>2</sub>, CHONH<sub>2</sub>, and ClO<sub>2</sub>. The decomposition behavior for DOAP has been reported by other investigators (Ref. 13).

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## **D. Oxidizer/Binder Prepolymer Compatibility**

(C) The compatibility of HAP, HP-2 and AP with UTREZ, UTREZ-diol, Telagen CT, R-45-M, Telagen-S EMD-590 and ethyl acrylate-acrylic acid copolymers (PU-105 and PU-103) were investigated. These polymers were selected for study on the basis of discussions with propellant formulators and suggestions from AFRPL. The prepolymers were used as received without further purification. All sample preparation was performed in a dry box having a dew point of -80°F.

(U) Approximately equal weights of the two ingredients (100 mg.) were used. The mixture was placed in a glass break-seal tube, evacuated and sealed. After standing in constant temperature baths for the reported time intervals, the samples were withdrawn and analyzed by IR, mass spectrometry and gas chromatography for gaseous decomposition products. Common gaseous decomposition products were N<sub>2</sub>, O<sub>2</sub>, CO, CO<sub>2</sub>, NO, and N<sub>2</sub>O. The sensitivity of the analytical techniques used to measure the concentrations of N<sub>2</sub>, O<sub>2</sub>, CO, and NO was 0.02 ml/g of oxidizer, while the sensitivity for CO<sub>2</sub> and N<sub>2</sub>O was 0.1 ml/g of oxidizer.

(U) The results of the analyses for gaseous decomposition products are given in Table V-II. The quantities reported were obtained by integrating the data obtained by IR spectroscopy, gas chromatography and mass spectrometry.

(U) Nitrogen is a common decomposition product of HP-2, while N<sub>2</sub>O is commonly observed from HAP. The evolution of these gases from mixtures of the oxidizers with other propellant ingredients is probably not attributable to oxidative degradation. The evolution of CO, CO<sub>2</sub> and possibly NO is indicative of oxidation reactions.

(U) The evolution of oxidation products from these mixtures is commonly accompanied by a darkening or charring of the prepolymers and in most cases by homopolymerization of the prepolymer. The homopolymerization may be due to oxidative crosslinking through olefin groups or chain extension by dehydration to form ethers or acid anhydrides.

(U) Residues of the oxidizer-binder prepolymer systems were retained for additional analysis utilizing infrared and wet chemical techniques. The intractable nature of these residues as well as their inherent sensitivity made the analyses difficult so that only very qualitative information could be obtained. Sample reproducibility was not attained; however, some general observation can be made.

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TABLE V-II

GASEOUS PRODUCTS FROM OXIDIZER-BINDER PREPOLYMER MIXTURES

<u>Oxidizer</u>	<u>Time (days)</u>	<u>Temp. (°C)</u>	<u>Gaseous Products (ml. gas/g oxidizers)</u>				
			<u>N<sub>2</sub></u>	<u>CO</u>	<u>CO<sub>2</sub></u>	<u>N<sub>2</sub>O</u>	<u>Others</u>
<u>UTREZ</u>							
HAP	31	25	-*	-	-	-	
		40	-	-	-	-	
		55	-	-	-	-	
		70	-	-	-	-	
	86	25	-	-	-	-	
		40	-	-	-	-	
		55	-	-	-	-	
		70	-	(t)	-	(t)	
	157	25	-	-	-	-	
		40	-	-	-	-	
		55	-	(t)	-	-	
		70	-	0.1	(t)	-	CH <sub>4</sub>
HP-2	49	25	-	-	-	-	
		40	-	-	-	-	
		55	-	-	-	-	
		70	-	-	-	-	
	91	25	-	(t)	0.6	-	CH <sub>4</sub>
		40	1.0	0.3	(t)	-	CH <sub>4</sub>
		55	2.7	0.3	0.3	-	CH <sub>4</sub>
		70	2.0	(t)	(t)	-	CH <sub>4</sub>
	162	40	0.8	(t)	-	-	CH <sub>4</sub>
		55	0.1	(t)	-	-	
		70	7.4	0.6	1.0	-	CH <sub>4</sub>
AP	141	70	-	-	-	-	
NONE	56	70	-	-	-	-	

\* (-) Denotes that no detectable quantities of the compound were found in the gaseous mixture.

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TABLE V-II (Continued)

<u>Oxidizer</u>	<u>Time (Days)</u>	<u>Temp. (°C)</u>	<u>Gaseous Products (ml. gas/g oxidizer)</u>				
			<u>N<sub>2</sub></u>	<u>CO</u>	<u>CO<sub>2</sub></u>	<u>N<sub>2</sub>O</u>	<u>Others</u>
<u>UTREZ-diol</u>							
HAP	45	25	-	-	-	-	-
		40	-	-	-	-	-
		55	-	-	-	-	-
		70	-	-	(t)	-	-
102	102	25	-	-	-	-	-
		40	-	-	-	-	-
		70	-	-	-	-	-
420	420	25	-	-	-	-	Hydrocarbon
		40	-	-	-	-	-
		55	-	tr	tr	tr	Hydrocarbon
		70	-	tr	tr	tr	Hydrocarbon
HP-2	49	25	-	-	-	-	-
		40	-	-	-	-	-
		55	-	-	-	-	-
		70	30.0	0.6	0.4	-	-
103	103	25	-	-	-	-	-
		40	-	-	-	-	-
		55	-	-	-	-	-
		70	0.5	(t)	(t)	-	-
AP	76	70	2.0	0.2	-	-	-
		25	-	-	-	-	Hydrocarbon
		40	-	-	-	-	Hydrocarbon
		55	-	-	-	-	Hydrocarbon
		70	-	-	-	-	Hydrocarbon
None	43	70	-	-	-	-	-

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TABLE V-II (Continued)

<u>Oxidizer</u>	<u>Time (days)</u>	<u>Temp. (°C)</u>	<u>Gaseous Products (ml. gas/g. oxidizers)</u>				
			<u>N<sub>2</sub></u>	<u>CO</u>	<u>CO<sub>2</sub></u>	<u>N<sub>2</sub>O</u>	<u>Others</u>
<u>EMD-590</u>							
HAP	49	70	-	-	-	-	-
	89	25	-	(t)	-	-	-
		40	-	-	-	-	-
		55	-	-	-	-	-
		70	-	0.5	(t)	-	-
HP-2	45	70	-	0.2	(t)	-	-
	86	25	-	(t)	-	-	-
		40	-	(t)	-	-	-
		55	-	0.1	(t)	-	-
		70	0.1	0.4	0.1	-	-
<u>TELAGEN-CT</u>							
HAP	49	25	-	-	(t)	-	-
		40	-	-	(t)	-	-
		55	-	-	-	-	-
		70	-	-	0.1	(t)	-
	84	25	-	-	(t)	-	-
157	84	40	-	-	(t)	-	-
		55	-	-	(t)	0.3	-
		70	-	-	0.2	-	-
	157	25	-	-	-	-	-
		40	-	-	-	-	-
HP-2	48	55	-	-	-	-	-
		70	-	-	-	-	-
	84	25	-	-	-	-	CH <sub>4</sub>
		40	-	-	-	-	CH <sub>4</sub>
		55	-	-	-	-	CH <sub>4</sub>
		70	-	-	-	-	CH <sub>4</sub>
		84	0.8	0.1	0.4	-	-

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TABLE V-II (Continued)

<u>Oxidizer</u>	<u>Time (days)</u>	<u>Temp. (°C)</u>	<u>Gaseous Products (ml. gas/g oxidizer)</u>				
			<u>N<sub>2</sub></u>	<u>CO</u>	<u>CO<sub>2</sub></u>	<u>N<sub>2</sub>O</u>	<u>Others</u>
154	25	-	-	-	-	-	-
	40	-	-	-	-	-	-
	70	-	-	-	-	-	-
AP	141	70	-	-	-	-	-
<u>R-45M</u>							
HAP	36	25	-	-	-	-	-
		40	-	-	-	-	-
		55	-	-	-	-	-
		70	-	-	-	-	-
	70	25	-	-	-	-	-
		40	-	-	-	-	-
		55	-	-	-	-	-
		70	-	(t)	-	(t)	-
	156	25	-	-	-	-	-
		40	-	-	-	-	-
		55	-	-	-	-	-
		70	-	-	(t)	-	-
HP-2	36	25	-	-	-	-	-
		40	-	-	-	-	-
		55	-	-	-	-	-
		70	-	-	-	-	-
	71	25	-	-	-	-	-
		40	-	-	-	-	-
		55	-	-	-	-	-
		70	-	(t)	-	-	-
	147	25	-	-	-	-	-
		40	-	-	-	-	-
		55	-	-	-	-	-
		70	1.6	0.1	0.1	-	-
AP	141	70	-	-	-	-	CH <sub>4</sub>

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TABLE V-II (Continued)

<u>Oxidizer</u>	<u>Time (days)</u>	<u>Temp. (°C)</u>	<u>Gaseous Products (ml. gas/g oxidizer)</u>				
			<u>N<sub>2</sub></u>	<u>CO</u>	<u>CO<sub>2</sub></u>	<u>N<sub>2</sub>O</u>	<u>Others</u>
<u>TELAGEN-S</u>							
HAP	60	70	-	-	-	-	-
	101	25	-	-	-	-	-
		40	-	-	(t)	-	-
		55	-	-	(t)	-	-
		70	-	-	0.1	-	-
HP-2	55	70	0.1	-	-	-	-
	98	25	-	-	-	-	-
		40	-	-	-	-	-
	101	55	-	-	-	-	-
		70	0.7	(t)	-	-	-
<u>PU-103</u>							
AP	28	25*			No gaseous products		
		40*			No gaseous products		
		60*			No gaseous products		
		80*			No gaseous products		
	70	25*			No gaseous products		
		40*			No gaseous products		
		60*			No gaseous products		
		80*			No gaseous products		
	177	25*			No gaseous products		
		40*			No gaseous products		
		60*			No gaseous products		
		80*			No gaseous products		
HAP	30	25*			No gaseous products		
		40*			No gaseous products		
		60*			No gaseous products		
		80*	-	-	tr	tr	Et <sub>2</sub> O; C <sub>2</sub> H <sub>4</sub>

\* Average value for duplicate samples.

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TABLE V-II (Concluded)

<u>Oxidizer</u>	<u>Time (days)</u>	<u>Temp. (°C)</u>	<u>Gaseous Products (ml. gas/g oxidizer)</u>				
			<u>N<sub>2</sub></u>	<u>CO</u>	<u>CO<sub>2</sub></u>	<u>N<sub>2</sub>O</u>	<u>Others</u>
74	25*			No gaseous products			
	40*			No gaseous products			
	60*		-	-	-	-	Et <sub>2</sub> O
	80*	tr	0.1	0.2	0.3		Et <sub>2</sub> O; C <sub>2</sub> H <sub>4</sub>
177	25*			No gaseous products			
	40*			No gaseous products			
	60*		-	-	-	-	Et <sub>2</sub> O
	80*	-	tr	0.2	0.6		Et <sub>2</sub> O; C <sub>2</sub> H <sub>4</sub>
<u>PU-105</u>							
AP	29	25*		No gaseous products			
		40*		No gaseous products			
		60*		No gaseous products			
		80*		No gaseous products			
66	25*			No gaseous products			
		40*		No gaseous products			
		60*		No gaseous products			
		80*		No gaseous products			
172	25*			No gaseous products			
		40*		No gaseous products			
		60*		No gaseous products			
		80*		No gaseous products			
HAP	30	25*		No gaseous products			
		40*		No gaseous products			
		60*	-	-	2.0	-	Et <sub>2</sub> O; C <sub>2</sub> H <sub>4</sub>
		80*	-	tr	1.0	-	Et <sub>2</sub> O; C <sub>2</sub> H <sub>4</sub>
70	25*			No gaseous products			
		40*		No gaseous products			
		60*	-	-	-	-	Et <sub>2</sub> O
		80*	0.5	0.2	0.5	0.6	Et <sub>2</sub> O; C <sub>2</sub> H <sub>4</sub>
171	25*			No gaseous products			
		40*		No gaseous products			
		60*	-	tr	tr	-	C <sub>2</sub> H <sub>4</sub> ; Et <sub>2</sub> O
		80*	tr	0.5	0.5	1.9	C <sub>2</sub> H <sub>4</sub> ; Et <sub>2</sub> O

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1. Carboxy terminated binders: UTREZ and Telagen (CT) are carboxy terminated polyisobutylene and polybutadiene, respectively. Both of these binder prepolymers appear to be slightly more susceptible to oxidative degradation than were their hydroxy terminated analogs.

Both carboxy terminated binder prepolymers homopolymerize in the presence of either HAP or HP-2 and are converted to brown-black solids at 40°C in a period of 30 to 60 days. This homopolymerization presents a situation of incompatibility accompanied by the absence of appreciable gas evolution. Possible reactions occurring include end group reaction, chain scission to produce methane, oxidative cross-linking and dehydration to form acid anhydrides.

The detection of methane as a gas phase reaction product together with the darkening or charring of the binder indicates attack on the polymer backbone which would logically result in radical or oxidative polymerization. However, the unsaturated Telagen (CT) should be much more susceptible to oxidative polymerization than UTREZ. Since little or no difference was noted in the rates of polymerization of the two materials, we conclude that dehydration to the acid anhydride must account for most of the observed reaction. Because of the nature of these solid residues, it is extremely difficult to unequivocally demonstrate which of the aforementioned reactions are occurring.

2. Hydroxy terminated binders: The compatibility of four hydroxy terminated resins with HAP, HP-2, and AP has been investigated. The prepolymers included UTREZ-diol, a polyisobutylene polymer; R-45M, EMD-590 and Telagen-S, polybutadiene polymers.

In general, these materials are slightly less susceptible to oxidative degradation than are the corresponding carboxy terminated materials. Little gassing was detected in all of these samples at 25, 40, and 55°C. At 70°C some oxidative degradation occurred in most systems. The one sample of UTREZ-diol and HP-2 contained a large quantity of nitrogen. Although it is suspected that the nitrogen was due to an air leak, no oxygen was present; and the amount of Cu and CO<sub>2</sub> found was not sufficient to account for the oxygen. However, the CO and CO<sub>2</sub> content was higher than that of samples which had been held at the same temperature for even longer time interval.

The hydroxy terminated prepolymers also homopolymerized in the presence of the oxidizers. R-45M solidified at 40°C in 92 days in the presence of HAP, while HP-2 turned R-45M to a brown solid in 36 days at 25°C. EMD-590 behaved in a very similar manner. UTREZ-diol and Telagen (S) appeared to be less susceptible to homopolymerization in the presence of the oxidizers than either R-45M or EMD-590; however, both turned to brown solids after longer time intervals or at higher temperatures.

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Previous studies at MRI (Ref. 10) and in other laboratories (Ref. 11) have shown that both HAP and HP-2 will dehydrate hydroxylated compounds to form ethers and/or olefins. This may account for the solidification of the binder prepolymers. In curing, the reactive end groups are removed and only backbone oxidation, oxidative cross-linking and cure linkage degradation are important storage stage binder reactions.

Infrared spectra of the residues from the oxidizer-prepolymer mixtures showed the presence of ammonium ions in both HAP and HP-2 samples. The ammonium ion arises from the decomposition of the hydroxylammonium and hydrazinium ion in HAP and HP-2, respectively. Quantitative data on the relative amounts could not be obtained from the spectra. No chemical changes in the prepolymer could be detected.

Wet chemical analysis of the residues was not satisfactory. We attempted to leach out the oxidizers from the residue and analyze for perchlorate and acid. Analyses gave a scatter of points indicating that leaching with water was not sufficient to extract all the oxidizer. Attempts to extract the binder from the oxidizer also resulted in incomplete solution of the oxidizer. In general, however, it appeared that the oxidizer remained essentially unchanged. This observation is similar to those reported in earlier studies (Ref. 10).

In summary, then, the oxidizer-binder prepolymer systems gave rise to intractable materials which could not be analyzed with any accuracy. These intractable solids may result from dehydration, chain scission (as indicated by methane formation) oxidative cross-linking or other end group reactions. It appears that ammonium ion may be present in these materials, but in small amounts. However, the oxidizer is probably basically unchanged and degraded only slightly. This must be considered as a situation of incompatibility capable of resulting in serious formulation or storage problems.

3. Ethyl acrylate-acrylic acid prepolymers: Studies on the compatibility of HAP and AP with two ethyl acrylate-acrylic acid copolymers initiated much later than the previously described studies. The two materials designated PU-103 and PU-105 were supplied by the Rohm and Haas Company. The ratios of ethyl acrylate to acrylic acid were 95:5 for PU-105 and 93:7 for PU-103.

Binary mixtures of the acrylates with HAP and AP were prepared in glass break-seal tubes in the same manner as described for the other oxidizer compatibility studies. The results obtained for the individual gaseous products from these mixtures are shown in Table V-II. Figure V-4 summarizes the total volume of gaseous products observed as a function of time for the HAP/PU-105 mixture at 80°C. Previous data for HAP/UTREZ(CT) and HAP/Telogen(CT) are included for comparison purposes.

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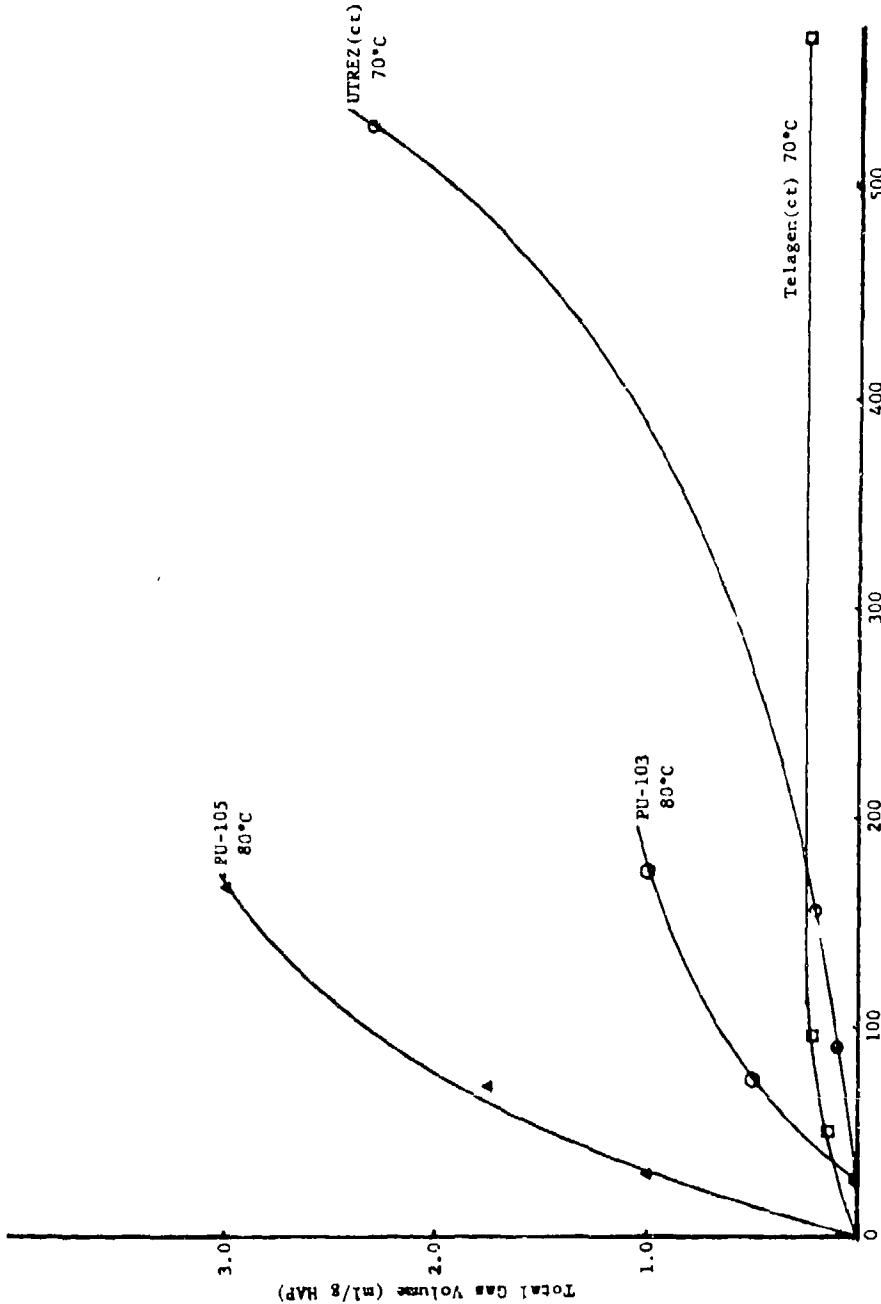


Figure V-4 - HAP-Binder Prepolymer Compatibility

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Data from the PU-103/HAP and PU-105/HAP studies showed no gas evolution after 177 days at temperatures up to 40°C. At 60°C, the PU-103/HAP mixture produced no gaseous decomposition products after 30 days, but did yield diethyl ether after 74 and 177 days. The system of PU-105 and HAP showed diethyl ether, ethylene, and trace quantities of CO and CO<sub>2</sub> after 171 days at 60°C. After approximately 170 days at 80°C, both acrylate/HAP systems showed the evolution of small quantities of gaseous decomposition products, including diethyl ether and ethylene. The formation of diethyl ether and ethylene is attributed to hydrolysis either of residual ethyl acetate solvent or the ethyl ester group in the binder prepolymer. These products, particularly ethanol, have previously been shown to react with HAP to form diethyl ether and ethylene (Ref. 10). The prepolymer binder appears to be slightly more susceptible to oxidative attack than is UTREZ or the Telagens. The formation of ethylene and diethyl ether should not be considered to be a deterrent in using this binder in conjunction with HAP since these results were obtained at temperatures much higher than would be encountered during propellant formulation or storage.

The acrylate binder prepolymers present no serious compatibility problems with the oxidizers under conditions commonly encountered by propellants. The formation of ethylene and/or diethyl ether is attributed to hydrolysis of residual ethyl acetate solvent or of the ethyl ester groups in the polymer to form ethanol. Ethanol in the presence of HAP dehydrates to form ethylene and/or diethyl ether.

### E. Oxidizer/Curing Agent Compatibility

Curing agents selected for study on this program include the isocyanates TDI, DDI, CTI, and epoxy (ERLA-4221) and an aziridine (MAPS). Again, the curing agents were selected on the basis of demonstrated utility in formulating propellants.

Gaseous decomposition products formed when mixtures of these curing agents with the oxidizers were allowed to stand at 25, 40, 55, and 70°C for various time intervals are shown in Table V-III.

The curing agents, most probably due to their inherent reactivity, are much more susceptible to oxidative degradation than are the binder prepolymers. They also homopolymerize in the presence of the oxidizers to give solids.

TDI is the most reactive of the isocyanates studied. CTI is the least reactive of the three studied. All of the isocyanates homopolymerize rapidly to form a coating around the oxidizer particles.

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TABLE V-III  
GASEOUS PRODUCTS FROM OXIDIZER-CURING AGENT MIXTURES

<u>Oxidizer</u>	<u>Time (days)</u>	<u>Temp. (°C)</u>	<u>Gaseous Products (ml. gas/g oxidizer)</u>				
			<u>N<sub>2</sub></u>	<u>CO</u>	<u>CO<sub>2</sub></u>	<u>N<sub>2</sub>O</u>	<u>Others</u>
<u>DDI</u>							
HAP	48	25	-*	-	(t)	-	-
		40	-	-	(t)	-	-
		55	-	-	(t)	-	-
		70	-	-	15.0	-	-
	67	25	-	-	(t)	-	-
		40	-	-	(t)	-	NO
		55	-	-	3.0	-	-
		70	1.0	0	22.0	(t)	-
	144	40	-	-	4.4	-	-
		55	-	-	14.2	1.6	-
		70	8.4	(t)	20.6	1.3	-
	406	25	-	-	2.2	-	-
		40	-	-	2.2	-	-
		55	-	-	-	-	-
		70	25.6	tr	41.6	2.0	-
HP-2	44	25	-	-	1.5	-	-
		40	-	-	3.0	-	-
		55	-	-	3.0	-	-
		70	-	-	6.0	-	-
	68	25	-	(t)	2.5	-	-
		40	-	(t)	7.0	-	-
		55	-	(t)	9.2	-	-
		70	-	0.03	10.5	-	-
	142	25	-	0.1	3.6	-	-
		40	-	-	4.5	-	-
		70	-	-	24.0	-	-

\* (-) Denotes that no detectable quantities of the compound were found in the gaseous mixture.

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TABLE V-III (Continued)

<u>Oxidizer</u>	<u>Time (days)</u>	<u>Temp. (°C)</u>	<u>Gaseous Products (ml. gas/g oxidizer)</u>				
			<u>N<sub>2</sub></u>	<u>CO</u>	<u>CO<sub>2</sub></u>	<u>N<sub>2</sub>O</u>	<u>Others</u>
AP	141	70	-	-	-	-	-
	378	25	-	-	0.3	-	-
		40	-	tr	0.4	-	Acetone
		55	-	0.4	0.9	-	-
DOAP	11	25	-	tr	3.7	-	-
		40	-	-	2.4	-	-
	8	60	tr	0.4	8.6	tr	CH <sub>3</sub> NO <sub>2</sub> , HCN
		80	0.5	1.3	27.1	1.2	HCN
33	33	25	-	-	2.5	-	-
		40	-	-	2.9	-	CCl <sub>4</sub>
		60	0.4	1.0	19.5	-	-
		80	3.6	1.8	76.2	2.6	HCN, CCl <sub>4</sub>
61	61	25	-	-	3.0	-	-
		40	-	0.26	6.4	-	-
		60	0.77	1.9	24.6	-	HCN
		80	8.57	2.3	54.7	-	HCN
None	53	70	-	-	-	-	-
			<u>TDI</u>				
HAP	64	70	1.1	0.4	70.0	8.0	-
		110	0.1	0.1	59.8	-	-
			0.1	0.1	43.2	0.3	-
			0.2	0.3	55.0	2.3	-
HP-2	62	70	1.8	0.6	96.0	5.7	-
		110	8.7	-	18.0	-	-
			(t)	-	8.7	-	-
			0.1	0.1	29.7	-	-
			1.2	1.1	80.0	-	-

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TABLE V-III (Continued)

<u>Oxidizer</u>	<u>Time (days)</u>	<u>Temp. (°C)</u>	<u>Gaseous Products (ml. gas/g. oxidizer)</u>				
			<u>N<sub>2</sub></u>	<u>CO</u>	<u>CO<sub>2</sub></u>	<u>N<sub>2</sub>O</u>	<u>Others</u>
DOAP	11	25	tr	tr	5.0	-	-
		40	-	-	3.8	-	Ester
	8	60	0.14	0.62	67.2	-	HCN
		80	0.95	7.2	12.5	-	HCN
	34	25	-	-	2.7	-	-
		40	-	tr	20.8	-	CCl <sub>4</sub>
		60	0.4	4.6	72.2	-	HCN
		80	0.5	6.1	82.8	-	-
	62	25	tr	tr	10.9	-	-
		40	tr	0.25	40.9	-	CCl <sub>4</sub>
		60	0.51	6.4	93.7	-	-
		80	0.31	15.9	160.0	-	-
<u>CTI</u>							
HAP	77	25	-	-	0.1	-	-
		40	-	-	0.2	-	-
		55	-	-	1.5	-	-
		70	1.7	-	8.3	1.1	NO
HP-2	76	25	-	-	1.3	-	-
		40	-	-	2.1	-	-
	83	55	-	-	2.5	-	-
		70	-	-	4.7	-	-
DOAP	8	25	-	-	tr	-	-
		40	-	-	14.3	-	-
		60	0.8	2.1	115.0	-	HCN
		80	1.1	3.0	66.0	1.3	HCN
	29	25	-	-	11.5	-	CCl <sub>4</sub>
		40	-	tr	11.8	-	-
		60	1.1	2.1	72.0	-	HCN
		80	2.0	3.1	122.0	-	-

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TABLE V-III (Continued)

<u>Oxidizer</u>	<u>Time (days)</u>	<u>Temp (°C)</u>	<u>Gaseous Products (ml. gas/g. oxidizer)</u>				
			<u>N<sub>2</sub></u>	<u>CO</u>	<u>CO<sub>2</sub></u>	<u>N<sub>2</sub>O</u>	<u>Others</u>
62	25	0.38	tr	26.1	-	-	
	40	0.35	0.18	22.8	-	-	
	60	0.56	3.1	79.9	-	-	
	80	4.21	3.65	104.0	2.5	HCN, CH <sub>4</sub>	
<u>HMDI</u>							
HAP	7	25	-	-	6.7	-	CCl <sub>4</sub>
		40	-	-	6.8	-	CCl <sub>4</sub>
8	60	0.6	-	8.1	-	CCl <sub>4</sub>	
		80	0.9	-	13.5	-	CCl <sub>4</sub>
28	25	-	-	5.07	-	CCl <sub>4</sub>	
	40	-	-	5.70	-	CCl <sub>4</sub>	
	60	0.22	-	13.2	-	CCl <sub>4</sub>	
	80	7.4	-	43.3	3.8	CCl <sub>4</sub>	
71	25	-	-	9.85	-	-	
	40	-	-	14.75	-	-	
	60	0.34	-	15.4	0.41	-	
	80	13.8	tr	61.6	7.49	-	
DOAP	7	25	-	-	4.4	-	CCl <sub>4</sub>
	40	-	-	6.6	-	-	
	60	tr	tr	16.7	-	HCN	
	80	0.2	0.2	42.0	-	HCN	
29	25	-	-	10.7	-	-	
	40	-	tr	9.4	-	-	
	60	-	-	26.8	-	-	
	80	-	-	51.5	-	HCN	
62	25	-	-	10.2	-	-	
	40	-	-	13.3	-	HCN	
	60	-	tr	17.7	-	-	
	80	2.1	0.53	86.3	1.7	HCN	

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TABLE V-III (Continued)

<u>Oxidizer</u>	<u>Time (days)</u>	<u>Temp. (°C)</u>	<u>Gaseous Products (ml. gas/g. oxidizer)</u>				
			<u>N<sub>2</sub></u>	<u>CO</u>	<u>CO<sub>2</sub></u>	<u>N<sub>2</sub>O</u>	<u>Others</u>
<u>PAPI</u>							
HAP	7	40	-	-	0.3	-	CCl <sub>4</sub>
		60	-	-	1.3	-	CCl <sub>4</sub>
		80	0.1	-	5.8	-	CCl <sub>4</sub>
	28	25	-	-	1.67	-	CCl <sub>4</sub>
		40	0.17	tr	4.89	-	-
		60	0.37	tr	10.7	2.40	CCl <sub>4</sub>
DOAP	7	25	-	-	6.5	-	-
		40	-	-	4.7	-	-
		60	0.3	0.6	37.4	-	HCN, CH <sub>4</sub>
		80	0.4	7.6	105.0	tr	CH <sub>4</sub>
	28	25	-	-	4.7	-	-
		40	-	tr	20.0	-	HCN
		60	0.6	1.8	58.3	-	HCN
		80	0.6	8.0	92.5	-	-
	62	60	2.1	6.8	138.0	-	-
		80	2.6	10.4	181.0	0.89	-
<u>ERLA-4221</u>							
HAP	46	25	-	-	-	-	-
		40	-	-	-	-	-
		55	-	-	-	-	-
		70	0.6	0.2	2.0	(t)	-
61	61	25	-	-	-	-	-
		40	-	(t)	(t)	(t)	-
		55	-	(t)	0.3	0.3	-
		70	-	-	5.3	0.3	-
133	133	25	-	-	-	-	-
		40	5.3	0.3	2.6	-	-
402	402	25	-	-	-	-	-
		40	-	-	-	-	-
		55	-	tr	1.0	-	-
		70	-	tr	2.3	-	-

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TABLE V-III (Continued)

Oxidizer	Time (days)	Temp. (°C)	Gaseous Products (ml. gas/g oxidizer)				
			N <sub>2</sub>	CO	CO <sub>2</sub>	N <sub>2</sub> O	Others
HP-2	45	25	-	-	-	-	-
		40	-	-	-	-	-
		55	-	-	-	-	-
		70	-	-	-	-	CH <sub>4</sub>
	62	25	-	-	(t)	-	-
		40	-	(t)	(t)	-	-
		55	0.1	0.1	0.7	-	-
		70	0.3	0.1	0.4	-	-
	132	40	-	-	-	-	-
		55	-	-	-	-	-
		70	0.3	0.3	3.7	-	-
AP	141	70	-	-	-	-	-
	354	25	-	-	-	-	-
		40	-	-	-	-	-
		55	-	-	-	-	-
	70	-	-	-	-	-	-
None	43	70	-	-	-	-	-
<u>MAPS</u>							
HAP	47	25	-	-	-	-	-
		40	-	-	-	-	-
		55	-	-	-	(t)	-
		70	-	-	0.4	1.8	-
	80	25	-	-	-	-	-
		40	1.0	0.3	-	(t)	-
		55	1.8	-	0.2	1.0	-
		70	3.7	0.05	0.8	5.0	-
159	25	(t)	-	-	-	-	-
	55	2.4	-	0.2	1.0	-	-
	70	3.2	0.3	0.8	4.4	-	-

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TABLE V-III (Concluded)

<u>Oxidizer</u>	<u>Time (days)</u>	<u>Temp. (°C)</u>	<u>Gaseous Products (ml. gas/g oxidizer)</u>				
			<u>N<sub>2</sub></u>	<u>CO</u>	<u>CO<sub>2</sub></u>	<u>N<sub>2</sub>O</u>	<u>Others</u>
HP-2	46	25	-	-	-	-	-
		40	-	-	-	-	-
		55	-	-	-	-	-
		70	-	-	0.1	-	-
	82	25	-	-	-	-	-
		40	-	(t)	-	-	-
		55	-	-	-	-	-
		70	38.0	-	0.2	-	-
	158	25	-	-	-	-	-
		40	-	-	-	-	-
		55	-	-	-	-	-
		70	20.6	0.6	0.6	-	-
AP	141	70	-	-	-	-	-
DOAP	7	25	0.3	-	-	-	-
		40	0.6	tr	-	-	-
		60	1.2	0.5	-	-	HCN
		80	2.8	1.5	-	-	Ether
	28	25	-	-	-	-	Ether
		40	-	-	-	-	HCN
		60	4.1	1.2	1.0	tr	HCN, Ether
		80	-	-	tr	-	Ether
	62	25	0.69	0.23	-	-	-
		40	1.0	0.42	-	-	HCN
		60	5.7	0.76	0.56	0.76	Ether
		80	-	-	2.13	0.76	Ether

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AP is considerably less reactive than HAP, HP-2 and DOAP with the isocyanates and does not cause DDI to homopolymerize at 70°C in 141 days or TDI at 70°C in 60 days. In general, HP-2 is considerably more reactive than HAP with the isocyanates.

The epoxy curing agent ERLA-4221 is less reactive than the isocyanates but more reactive than any of the binder prepolymers with the oxidizers. It also homopolymerizes rather rapidly in the presence of HAP and HP-2 but reacts little with AP. Homopolymerization to a solid occurred in the presence of HAP in 90 days at 25°C, in 30 days at 40° and within 5 days at 55° and 70°C. HP-2 caused homopolymerization in about the same time intervals at the respective temperatures. The oxidizers are more reactive with the isocyanate homopolymers than with the epoxy homopolymers.

The aziridine curing agent MAPS has not been used extensively to cure propellants containing HAP but has been used for HP-2 propellants. MAPS was found to be more compatible with HP-2 than with HAP. It appears to be compatible with HP-2 for a period of 158 days at 55°C. By comparison, MAPS promoted the decomposition of HAP and underwent some oxidative degradation in the presence of HAP under the same conditions. This aziridine appears to be sufficiently basic to promote the dissociation of both oxidizers at 70°C as evidenced by the quantities of N<sub>2</sub>O evolved from the HAP systems and N<sub>2</sub> evolved from HP-2 mixtures. AP showed little or no reactivity with MAPS at 70°C in 141 days although it did cause the curing agent to homopolymerize.

#### F. Oxidizer/Cured Binder Compatibility

Since the oxidizers are known to affect the rate and degree of cure of an isocyanate cured system (Ref. 16), it was decided to prepare a gum stock and study its compatibility with the two oxidizers to obtain a fair comparison. A cured binder sample was prepared from R-45M and DDI using recommended stoichiometry of the two reactants. When cured, the gum stock was cut into small pieces to expose a large surface area and then mixed with the oxidizers. The results obtained after approximately 90 days are shown in Table V-IV.

No reaction was observed at 25°C. Although no gaseous products could be detected at 40°C, it was apparent that some reaction was occurring because of an obvious darkening of the polymer. Gaseous products were detected at 55° and in larger quantities at 70°C. Considerable darkening or charring of the binder also occurred at the two higher temperatures. Since no excess isocyanate was employed in curing the binder, it appears that the urethane linkage is susceptible to degradation in the presence of the oxidizers.

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TABLE V-IV

## OXIDIZER COMPATIBILITY WITH BINDERS

<u>Binder</u>	<u>Oxidizer</u>	<u>Time (days)</u>	<u>Temp. (°C)</u>	Gaseous Products (ml. gas/g oxidizer)				
				<u>N<sub>2</sub></u>	<u>CO</u>	<u>CO<sub>2</sub></u>	<u>N<sub>2</sub>O</u>	<u>Other</u>
R-45M/DDI	HAP	91	25	-	-	-	-	-
			40	-	-	-	-	-
			55	-	tr	2.5	-	-
			70	-	0.7	6.0	2.8	-
R-45M/DDI	HP-2	89	25	-	-	-	-	-
			40	-	-	-	-	-
			55	-	-	tr	-	-
			70	1.3	1.1	5.5	-	-
$C_2H_5NHC(O)OC_2H_5$	DOAP	8	25	-	-	1.8	-	-
			40	-	-	3.1	-	-
			60	1.2	tr	70.4	tr	HCN
			80	-	-	24.3	-	HCN
	28	25	-	-	1.4	-	-	-
			40	-	-	4.3	-	Ester
			60	1.1	-	39.4	-	Ester
			80	5.9	0.4	83.3	5.3	Ester
	62	25	-	-	1.7	-	-	-
			40	-	-	26.5	-	Ester
			60	0.7	tr	44.1	1.7	Ester
			80	5.0	0.1	108.0	4.1	Ester

## G. Whole Propellant Studies

In addition to the study of ingredient reactivity and stability under formulation and cure conditions, another major aspect of the evaluation of a propellant (and its components) is the assessment of its aging characteristics. While an understanding of the long-term behavior of ingredients and their mixtures is important to an aging study, completeness and accuracy require an examination of the whole propellant by techniques which will yield data which can be related to such aging phenomena as changes in mechanical properties, burn rate, etc.

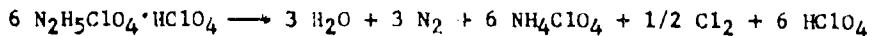
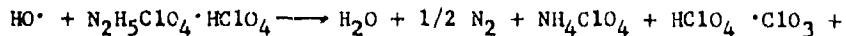
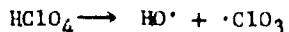
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(U) A study of storage and aging was performed with a propellant grain furnished by Thiokol Chemical Corporation. The propellant consisted of a mixture of HP-2 and aluminum with a carboxyl-terminated polybutadine binder. The system was aziridine-cured (MAPO or BITA) and contained approximately 3% polybutene as well as small quantities of an antioxidant. Samples were stored under a variety of conditions, including a series of sealed tubes under vacuum at 25, 40, 55, or 70°C for 280 days. Others were stored at ambient conditions in a dry box and examined at various time intervals. DTA and gas evolution measurements showed little or no differences among the samples. The most results came from mass spectrometric pyrolysis studies on the ambient/dry box stored material. These results are summarized in Figures V-5 through V-8.

(C) In Figure V-5, curve series A represents the data observed in October 1968 for a sample of the propellant stored for approximately 6 months in a dry box at ambient. Curve series B is representative of a sample of the same propellant pyrolyzed in the mass spectrometer after 10 months of similar storage (ambient/dry box). The m/e values presented in Figure V-5 are not the only ones observed but are representative of the major aspects of the decomposition reaction. The ion at m/e 67 is representative of perchloric acid evolution and m/e 32 is attributed to hydrazine. These results show a significant difference between the two samples of the same propellant. Variations in peak intensity between the two runs are not relevant because of variable sample size; however, the rate of evolution with temperature is quite significant. For curve A, the data are as would be expected for the decomposition of pure HP-2 (in a propellant matrix), that is, very little dissociation (other than  $\text{HClO}_4$ ) until 140-150°C (Ref. 14). In contrast, curve B shows the rapid evolution of products at temperatures considerably lower than that expected for HP-2. Such an observation is indicative of gross changes in the HP-2 present in the propellants.

(U) It is interesting to speculate about the nature of this change. The presence of a large amount of hydrazine (relative to perchloric acid and other decomposition species) is not expected from HP-2 decomposition; perchloric acid formed from HP-2 will oxidize hydrazine to ammonia (which reacts further) and liberate another mole of perchloric acid according to the scheme shown below (Ref. 7):



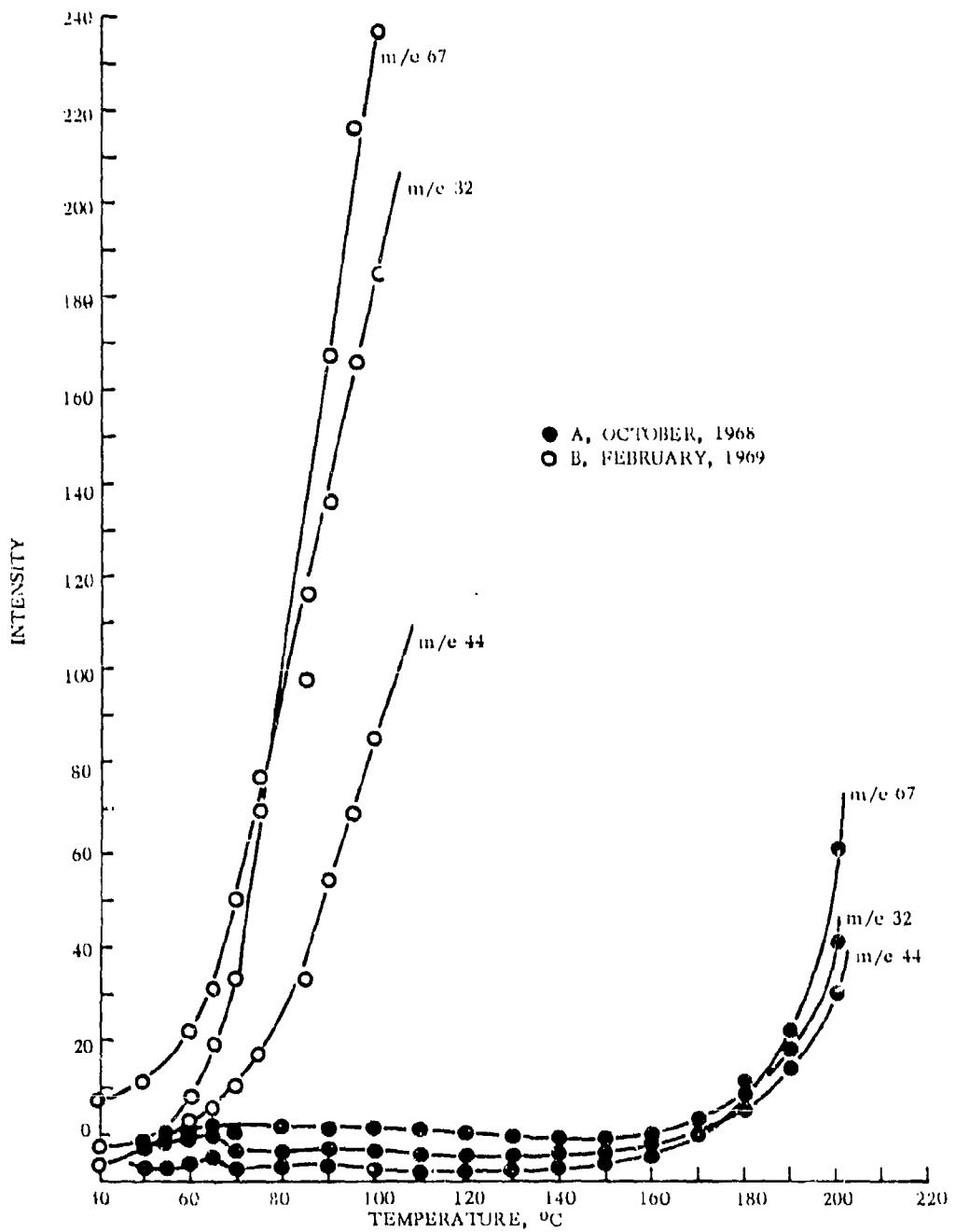


Figure V-5 - Partial Mass Spectrum of HP-2 Propellant from Thiokol

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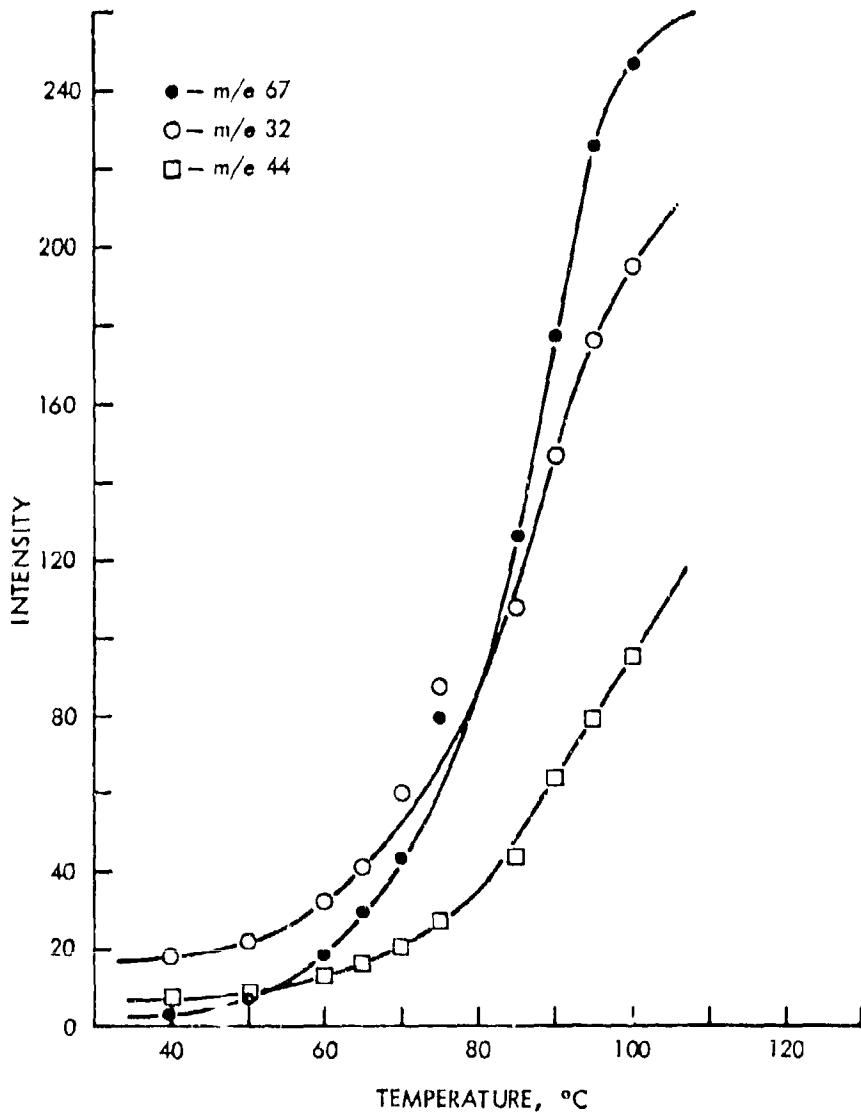


Figure V-6 - HP-2 Propellant from Thiokol After Standing at Ambient Temperature in Dry Box

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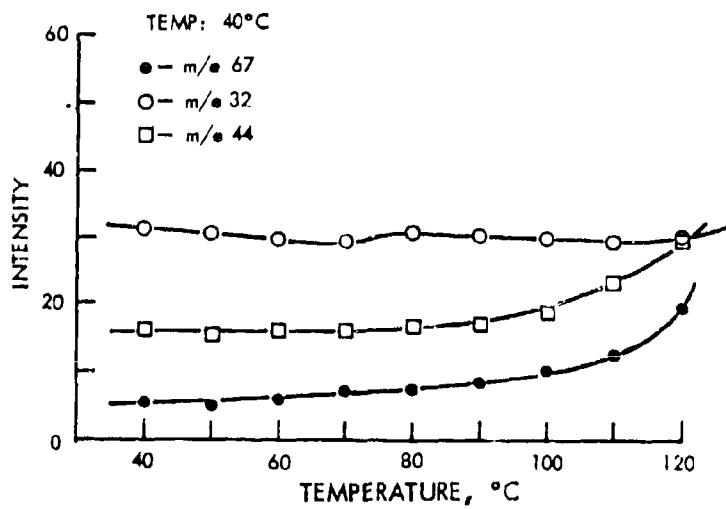
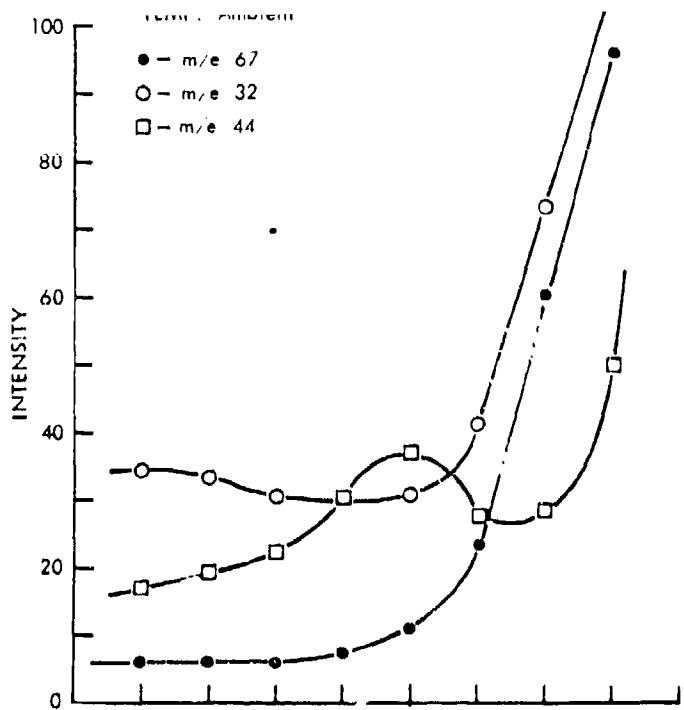


Figure V-7 - HP-2 Propellant After Aging at Ambient and 40°C

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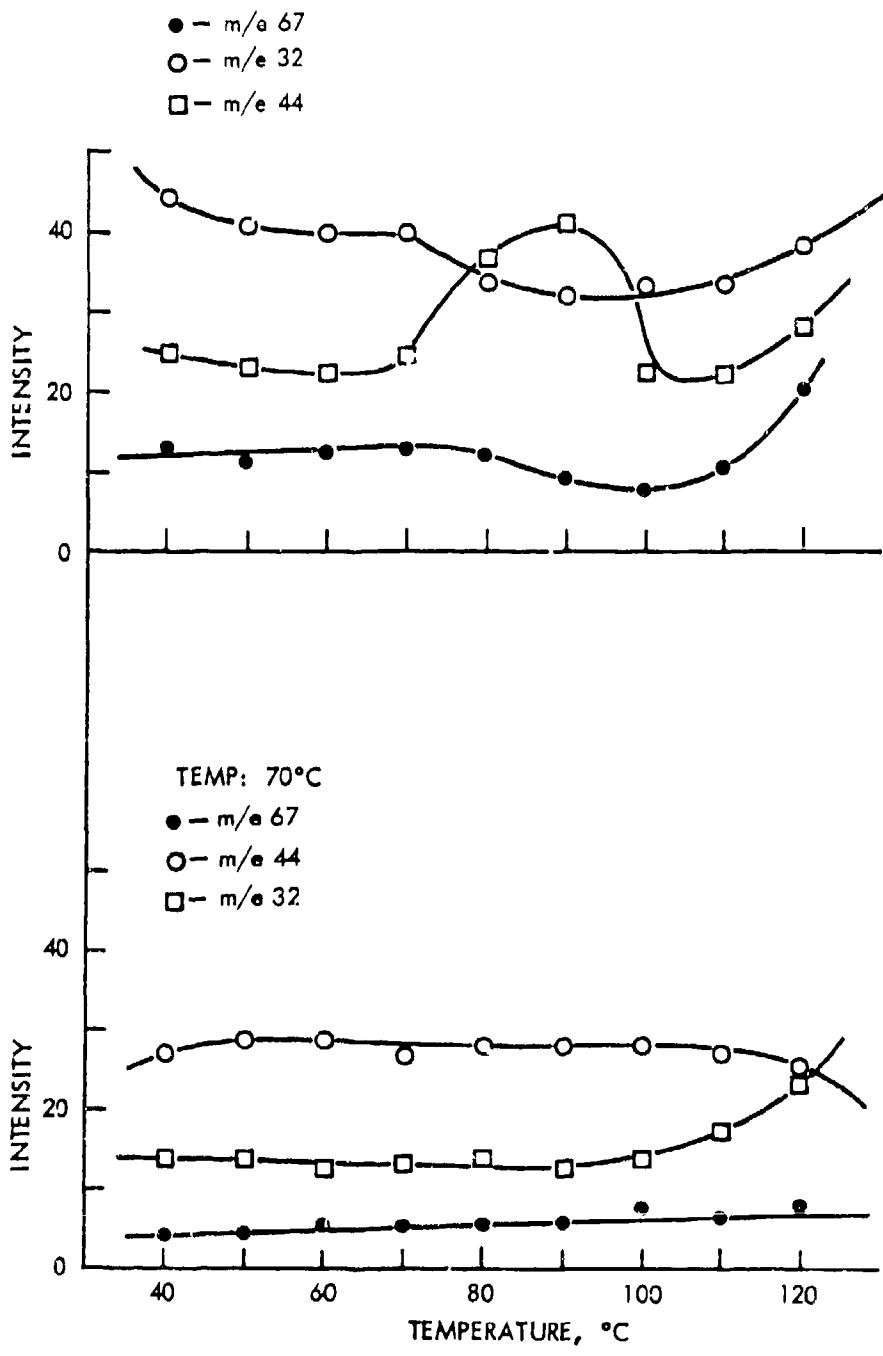


Figure V-8 - HP-2 Propellant after Aging at 55 and 70°C

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Hence, for hydrazine to survive, the perchloric acid must be reacting out via an alternative and competing pathway. In a propellant, the organic matrix provides such a route and the presence of m/e 44 ( $\text{CO}_2$ ) would tend to support this hypothesis (m/e 44 has been identified as  $\text{CO}_2$  rather than  $\text{N}_2\text{O}$  since the latter is not to be expected from HP-2 in such abundance). The origin of the  $\text{CO}_2$  can be attributed to the reaction of perchloric acid with the polymeric backbone or with the cure linkage. Hence, one aspect of the aging mechanism for this propellant involves liberation of the weakly held perchloric acid group from HP-2, reaction of this material with binder material and the resulting survival of hydrazine in the propellant. Hydrazine can act as a solvent for the oxidizer, hence changing its decomposition characteristics (rate and temperature of evolution). There are insufficient data to assign significance to the time periods involved (six months and 10 months).

Samples of the same propellant were stored in sealed tubes for 280 days at 25, 40, 55 and 70°C. These samples were then subjected to both EPR and mass spectrometric analysis. The ambient temperature results (Figure V-6) for the sample from the sealed tube experiment are in agreement with those from the ambient/dry box stored material (curve B, Figure V-5). The samples stored at elevated temperature, however, do not show as high a concentration of primary decomposition products (Figures V-7 and V-8) as do the ambient samples, indicating that these species ( $\text{N}_2\text{H}_4$ ,  $\text{ClO}_4^-$ ) are reacting out as the temperature is increased. One feature common to all the samples is the appearance of peaks in the following groups of m/e values: 261, 263, and 255; 162, 164, and 166; and 110-120 immediately after insertion of the sample into mass spectrometer. These values were in addition to those expected from hydrazine, perchloric acid, and the other normal gaseous products. The difference between the first two groups is almost assuredly due to the loss of perchlorate ion ( $\text{ClO}_4^-$ ); however, the mass is too high for the parent species to be HP-2. All these higher m/e species disappear 5 min. after insertion into the mass spectrometer. Such species most likely result from reactions occurring between  $\text{ClO}_4^-$  and the binder to produce organoperchlorates such as  $\text{C}_{12}\text{H}_{21-23}\text{ClO}_4$ .

The EPR spectra for these samples (Figure V-9) show an increase in signal intensity with temperature. The increasing EPR signal with temperature is to be expected for the increasing reaction of perchloric acid (through species such as  $\text{HO}^\cdot$ ,  $\text{ClO}_3^\cdot$ ) with the binder material, reaction which would be radical in nature. A similar increase in signal intensity was noted as a function of time at constant temperature.

**H. Summary of Results**

Chemical changes, together with the identification and measurement of the rates of evolution of gaseous decomposition products, were investigated

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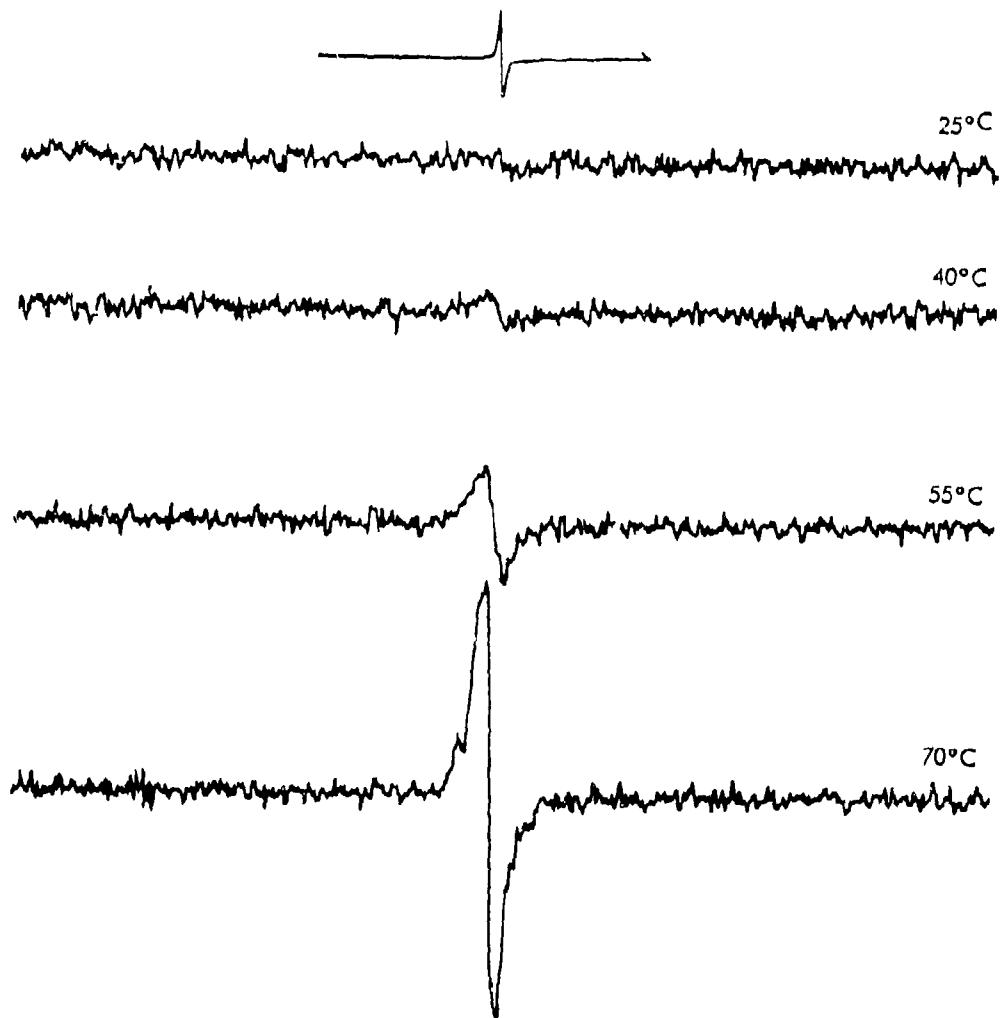


Figure V-9 - EPR Spectra of an HP-2 Propellant Stored at Four Temperatures

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To obtain a more definitive insight into the thermal stability of the oxidizers, HAP, HP-2, and DOAP, and their compatibility with selected binder prepolymers and curing agents. The results of this study are summarized in the following paragraphs.

1. Oxidizer stability: The thermal stability of HAP is good, though inferior to that of AP. Studies at 70°C in glass indicated only trace quantities of NO and N<sub>2</sub>O after 72 days. Mass spectrometric studies showed very little decomposition at temperatures up to 80°C.

The low temperature dissociation of HP-2 was observed in a mass spectrometric study. No gaseous decomposition products were detected by IR or GC analysis of an HP-2 sample stored at 70°C for 72 days.

A plot of log (ion intensity) vs. 1/T °K for three ions thought to be a direct result of HP-1 dissociation gave an average E<sub>a</sub> = 24.4 kcal/mole for the temperature range of 140 to 180°C. This value is in very good agreement with the literature value (Ref. 7).

2. Oxidizer/binder prepolymer compatibility: In general, it was found that the binder prepolymers utilized in this study were less reactive with the two oxidizers, HAP and HP-2, than were the curing agents. None of the prepolymers showed any substantial reaction with either oxidizer as evidenced by the fact that the most reactive combination (UTREZ + HP-2) produced ~ 9 ml. of total gaseous product at 70°C after 5 months.

a. UTREZ: HAP is less reactive than HP-2 at all four temperatures for time periods of 5 months. AP-UTREZ and UTREZ alone gave no evidence of reaction or decomposition at 70°C after 5 and 2 months, respectively.

b. UTREZ-diol: Neither HAP nor HP-2 undergoes any reaction at 55°C or lower for 3 months. After 3 months at 70°C, both oxidizers show very little reaction; HP-2 may be slightly more reactive. Only traces of gaseous products were detected from HAP-UTREZ-diol mixtures after 420 days, and none from AP-UTREZ-diol.

c. EMD-590: Both oxidizers produced very little reaction at any of the four temperatures for time periods of 3 months.

d. Telagen-CT: Neither oxidizer showed any appreciable reaction after 5 months at any of the temperatures. AP showed no reaction at any temperature for 5 months.

e. Telagen-S: Very little reaction occurred with either oxidizer at any temperature after 3 months.

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(U) f. R-45H: After 5 months at the three lower temperatures, neither oxidizer produced any gaseous products. At 70°C, HP-2 evolved ~ 2 ml. of total gaseous product per gram of oxidizer in 5 months. AP produced only a trace of methane after 5 months at 70°C.

(U) g. Acrylates: There is little apparent difference in the stability of the two acryl-te binders studied. What gassing is observed in the presence of the oxidizers is attributed to residual ethyl acetate solvent present in the high molecular weight and hence, very viscous prepolymer.

(U) h. Oxidizer/binder residue: Qualitative analysis of the residues from the oxidizer/binder mixtures by IR showed the presence of small quantities of ammonium ions from both HAP and HP-2. However, the major portion of each of the components remained essentially unchanged.

(U) 3. Oxidizer/curing agent compatibility:

(U) a. DDI: For time periods of 144 days at 25, 40, and 55°C, HAP and HP-2 appear to have about the same degree of reactivity. At 70°C and for the same time period, HAP is more reactive than HP-2. AP was found to be completely unreactive over the same time interval. The neat curing agent evolved no gases in 53 days at 70°C.

(U) b. TDI: HAP is more reactive than HP-2 at all four temperatures after 110 days.

(U) c. CTI: At the three lower temperatures, HAP was found to be slightly less reactive than HP-2 for an 80 day time interval. However, at 70°C, HAP was more reactive for the same time span.

(U) d. HMDI: HAP reacted extensively with HMDI at all temperatures and all time intervals studied.

(C) e. PAPI: DOAP was more reactive with PAPI than was HAP.

(U) f. ERLA-4221: Neither HAP nor HP-2 exhibited a large amount of reactivity, as evidenced by gassing, with this epoxide. Both oxidizers caused the epoxide to polymerize.

(U) g. MAPS: HAP was found to be more reactive than HP-2 at the three lower temperatures over a 5 month interval. At 70°C, HP-2 was more reactive than HAP for time intervals of 3 and 5 months. After 5 months, AP produced no gaseous products at any of the four temperatures.

Towards HAP: All temperatures

CTI < DDI < PAPI < HMDI < TDI

Towards HP-2: All temperatures

CTI < DDI < TDI

Towards DOAP: All temperatures

DDI < HMDI < CTI ≤ PAPI, TDI

(C) 4. Oxidizer/cured binder compatibility: In studies of the compatibility of the oxidizers with a DDI cured R-45M binder, very slow urethane degradation was observed at 55-70°C, as evidenced by CO<sub>2</sub>, and CO generation. This evidence extrapolates (10 fold/10°C rate change) to 2-3% degradation of oxidizer in 5 years at 25°C. The extrapolation is crude, but is justification for concern that the physical properties of a propellant grain, formulated from these ingredients, would deteriorate significantly during storage.

(U) 5. Whole propellant studies: Mass spectrometric studies of an HP-2 propellant very clearly revealed phenomena, occurring at ambient conditions, which within 1 year are not necessarily catastrophic but portend certain failure. The phenomena lack complete definition in the mechanism sense and are in fact quite intriguing to the specialist in mechanisms; the phenomena are in keeping with observed characteristics of HP-2; of particular interest is the amount and type of information obtained by the mass spectrometric examination. HP-2 is an admittedly willing subject (Ref. 17), but one justifiably predicts that useful information can be gleaned from less willing (less reactive, more stable) systems. The industry needs techniques to handle the stable system.

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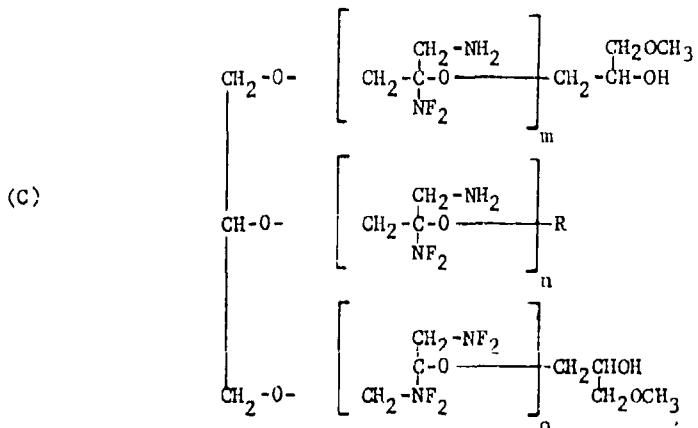
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VI.

STABILITY AND COMPATIBILITY OF P-BEP

A. Background

(C) P-BEP is prepared by Shell Development Company by direct addition of  $N_2F_4$  to poly(2,3-epoxypropane). The average structure of the prepolymer as proposed by Shell (Ref. 1) is:



$$m + n + o = 26 \text{ to } 30$$

R = nonfunctional termination

P-BEP is a highly viscous liquid with a typical number average molecular weight of 3,300 to 4,400. Fractionation of the polymer at UTC (Ref. 2) showed that approximately 10% of the polymer has a molecular weight of 5,500 or greater and 30% has a molecular weight below 2,800. The lowest molecular weight fraction ( $MW \sim 1,200$ ) isolated was reported to be much less stable than the higher molecular weight fractions.

(C) Studies on the slow thermal decomposition of P-BEP performed at Dow Chemical Company (Ref. 3) on Shell Lot No. 9557-82, ( $MW = 3,670$ ) gave HF, HCN,  $N_2$ ,  $CO_2$ , and  $N_2F_4$  as the principal gaseous decomposition products at  $150^\circ$  and  $160^\circ C$ , with minor quantities of  $NF_3$ ,  $N_2F_2$ ,  $^1F_2$ , and  $N_2O$ . Mass spectrometric analysis of the solvent from "as-received" P-BEP indicated the presence of n-pentane, 2-methylbutane, acetone, pentene, and hexane as contaminants. Total gas-evolution measurements showed  $\sim 220$  cc. of gas evolved per gram of P-BEP in 4.5 hr. at  $150^\circ C$ . A 20% weight loss of P-BEP occurred at this temperature in the same time period.

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(U) Thermal stability studies on neat P-BEP (Lot 9165-107) performed at UTC (Ref. 4) showed that the polymer contained 0.5 to 2% methylene chloride. At 45 and 60°C, solvent loss, which was diffusion-controlled, continued for ~ 200 hr. The weight losses of neat P-BEP (containing 0.5 to 2% methylene chloride) were 0.25 to 0.30% in the 1,000 hr. at ambient temperature, 1.9% in 1,000 hr. at 45°C, and 4.8% in 1,000 hr. at 60°C. Part of the weight loss was attributed to solvent evaporation.

(C) Rapid pyrolysis studies have been performed on P-BEP at Lockheed Propulsion Company (Ref. 5). The procedure involves pyrolyzing the sample on a platinum ribbon located within 2 mm. of the ionizing electron beam in a Bendix time-of-flight, Model 12-101, mass spectrometer. The heating rates commonly employed were in the range of hundreds of degrees per second. The initial ion fragments detected were  $C_3H_4^+$ ,  $C_2H_3O^+$ ,  $C_2H_5O^+$ , and  $HCNF^+$ . In their studies HF began to appear at about 60°C.

(C) The results of previous studies on the stability of P-BEP clearly indicate that a more definitive picture of the mode and rate of its decomposition is needed, particularly under conditions which would be employed in formulating a propellant using a P-BEP binder.

(C) Studies performed on this program were designed:

- (1) to determine the types of decomposition P-BEP undergoes at propellant processing temperatures;
- (2) to determine the rate of decomposition as a function of temperature; and
- (3) to determine, if possible, the temperatures at which the various modes of decomposition are initiated.

(C) In addition, the compatibility of P-BEP with AP and the energetic oxidizers HAP and HP-2 was investigated. These studies were designed to identify formulation problems which might develop in preparing propellants containing these energetic ingredients, and to obtain information on the storability of such propellants.

(C) Studies were performed on the compatibility of P-BEP with the curing agents.

(C) The compatibility of P-BEP with  $AlH_3$  was investigated and a significant effort was devoted to methods of stabilizing this combination of energetic ingredients. That portion of the program is discussed in Section VII.

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**B. P-BEP Purification and Handling**

Two lots of P-BEP have been used in these studies. All of the early work was performed on Lot No. 9557-82, while more recent work has been with Lot No. 10001-168. Shell submitted the following data on these samples: Lot No. 9557-82 was reported to have a number average molecular weight of 3,670 and a thermal stability of 4.6 cc. of gas liberated per gram of P-BEP per 100 hr. at 80°C. Sample No. 10001-168 had a number average molecular weight of 3,400 and a thermal stability of 5.2 cc. of gas liberated per gram of P-BEP per 100 hr. at 80°C. No difference in stability or compatibility was observed for the two samples in these studies.

The P-BEP used on this program was shipped as a methylene chloride solution. Proton NMR spectra of the as-received material indicated that the solution contained hydrocarbon impurities. These impurities were identified in a Dow report (Ref. 6) as n-pentane, 2-methylbutane, acetone, propene, and hexane. Since P-BEP was found to be relatively insoluble in Freon-11, all P-BEP used in these studies was purified by precipitating it from methylene chloride with Freon-11. Three successive precipitations were employed in this purification, which resulted in a loss of 10 to 15 wt. % of the P-BEP. It was reported by UTC that the low molecular weight fractions of the polymer are retained in Freon-11 solvent. Based on the weight loss observed and the molecular weight distribution reported by UTC (Ref. 2), this would indicate that the fraction removed would have molecular weights below 2,000. No evidence of hydrocarbon impurities could be detected by NMR in P-BEP purified by this procedure.

AP was obtained from G. Frederick Smith Chemical Company. The HAP used in these studies was furnished by the Elkton Division of Thiokol Chemical Company. Analysis of this oxidizer sample at MRI indicated a purity of about 98%. The HP-2 was furnished by the Wasatch Division of Thiokol, and had a reported purity of 98.84%.

**C. Experimental Techniques**

The combined capabilities of IR, NMR, and ESR spectroscopy plus gas chromatography and mass spectrometry were employed on this study.

Infrared spectroscopy was used to continually monitor the quantities of infrared active gaseous decomposition products liberated from P-BEP as a function of time and temperature. A 100-mg. sample of P-BEP was placed in a stainless steel sidearm attached to a 10 cm. Kel-F infrared cell fitted with Wilber chloride windows. The entire cell was passivated with chlorine trifluoride for 2 hr. at 8 psig before placing the P-BEP in the sidearm and the entire system was evacuated at  $10^{-4}$  Torr for 2 hr. The sample was then

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heated with a small thermocouple controlled brass block heater regulated by a "limtrol" thermal regulator sensitive to  $\pm 1^{\circ}\text{C}$ . A Beckman Model IR-12 infrared spectrophotometer scanned the spectral region 700-3,960  $\text{cm}^{-1}$  continually every 55 min. These scans were normally continued for 16 hr. After 16 hr., the gaseous decomposition products were analyzed by gas chromatography and mass spectrometry.

(C) Reasonably good measures of the quantities of residual methylene chloride, present in the sample, and of HCN, HF,  $\text{N}_2\text{O}$ ,  $\text{NF}_3$ , and  $\text{N}_2\text{F}_4$  liberated during the decomposition were obtained from infrared spectra. Gas chromatography yielded quantitative data on the  $\text{N}_2$ ,  $\text{O}_2$ , CO, NO,  $\text{CO}_2$ , and  $\text{N}_2\text{O}$  content of the gaseous decomposition products. A portion of the gaseous decomposition products were retained for mass spectrometric analysis to supplement and confirm other methods of analyses.

(U) For longer term studies, 100-mg. samples of P-BEP were placed in passivated stainless steel tubes, evacuated and immersed in constant temperature baths for the desired time intervals. When removed from the constant temperature baths, they were attached to the Kel-F infrared cells and the gaseous products analyzed by the procedures described in Section IV. Temperatures employed for these studies were 25°, 40°, 55°, and 70° and sometimes 85°C.

### **D. Experimental**

(U) 1. P-BEP characterization: F. A. Bovey (Ref. 7) described successful applications of NMR to polymer chemistry, i.e., the observation by NMR of the stereochemical configuration of vinyl polymers which is related to their crystallizability, softening or melting temperatures, and mechanical behavior. The principal advantage of magnetic resonance in molecular structure studies is its sensitivity to minute structural changes within molecules and to environmental effects on molecules. Because of this sensitivity and the availability of a number of accessory techniques, it is frequently possible to assign each of the absorptions of an MRI spectrum to a specific structural feature.

(U) The structural features of P-BEP have been examined by many investigators; however, combining all of this information does not yield a clear picture of the structure of P-BEP. Little has been done to define lot-to-lot variations and the relation of structure to curing characteristics, thermal stability, and chemical stability.

(U) A portion of this program was directed towards the examination of the molecular structure and reactions of P-BEP using a high resolution NMR spectrometer; the following is a discussion of the structural assignments as a result of that study.

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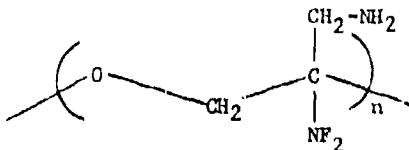
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(U) Figure VI-1 shows a portion of the 60 MHz (14,000 gauss)  $^1\text{H}$  NMR spectrum and the 100 MHz (23,500 gauss) spectrum of P-BEP in acetone-d<sub>6</sub>. The sharp absorption at lowest field (far left) in both  $^1\text{H}$  spectra is due to residual methylene chloride in the sample. The methylene chloride is a convenient internal reference for chemical shift measurements.

(U) Only four other absorptions are discernible in the 60 MHz spectrum and the presence of fine structure is difficult to evaluate because of the poor signal-to-noise ratio. On the other hand, at 100 MHz, a potentially far more informative spectrum of P-BEP is obtained. This is because both resolving power and sensitivity in magnetic resonance are proportional to magnetic field strength.

(U) The observed  $^1\text{H}$  peak positions measured from internal methylene chloride in acetone at 60 and 100 MHz are listed in Table VI-1. These peak positions may be related to the universal reference tetramethylsilane by applying the appropriate correction (see footnote to Table VI-1).

(C) The broad peak at 0.94 ppm is the strongest absorption in the spectrum of P-BEP. This absorption is assigned to the methylene group hydrogens of the main or backbone chain of the molecule. The protons are not coupled



strongly to either the fluorines of the adjacent difluoramine group or the hydrogens of the side chain or branching methylene group.

(C) The absorption at 1.22 ppm is the center peak of a 1:2:1 triplet which is due to the side chain methylene hydrogens. The methylene signal is split into a triplet by coupling with the two fluorine nuclei of the side chain difluoramine group. The position of the center of the triplet is a function of magnetic field strength as expected for a chemical shift. However, the separation between the peaks of the triplet is independent of field strength, which verifies the splitting as due to nuclear spin-spin coupling. The separation between the peaks is 27 Hz which is the expected magnitude for vicinal H-F coupling.

(C) Structures 1-3 are model compounds having the  $\text{CH}_n\text{-NF}_2$  group.

The  $J_{\text{H}-\text{F}}$  values of these models are in the range of 20-30 Hz. This

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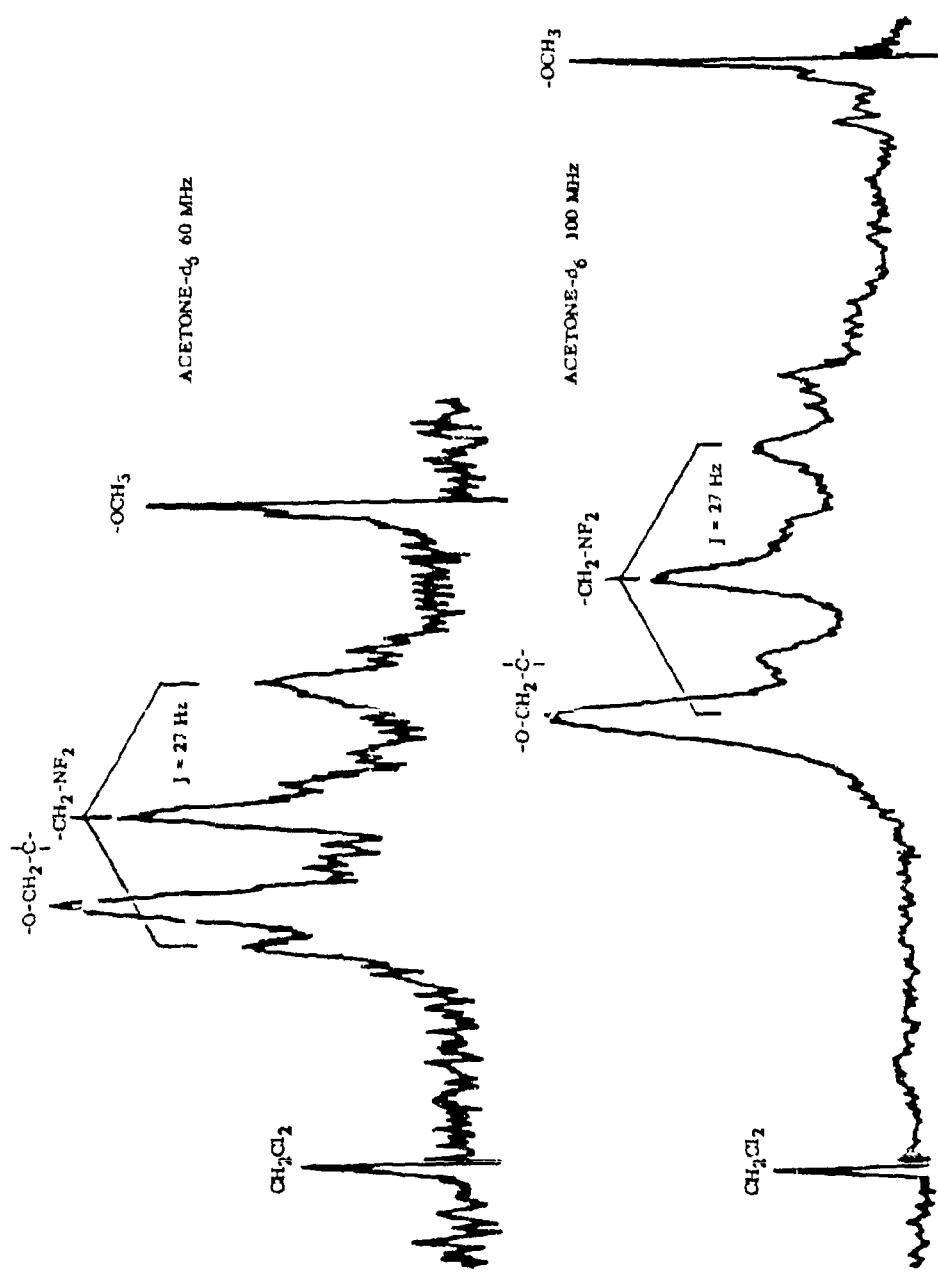


Figure VI-1 -  $^1\text{H}$  NMR Spectrum of P-BEP in Acetone- $d_6$

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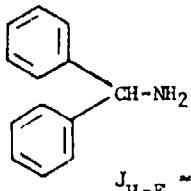
TABLE VI-I

<sup>1</sup> H NMR PEAK POSITIONS OF P-BEP IN ACETONE-d <sub>6</sub>				
AT 60 AND 100 MHz <sup>a/</sup>				
60 MHz (Hz)	60 MHz (ppm)	100 MHz (Hz)	100 MHz (ppm)	Assignment
0	0	0	0	CH <sub>2</sub> Cl <sub>2</sub>
46	0.766			-CH <sub>2</sub> -NF <sub>2</sub> triplet
54	0.90	94	0.94	-O-CH <sub>2</sub> -C- main chain
		106	1.06	Unknown
73	1.22	123	1.23	-CH <sub>2</sub> -NF <sub>2</sub> triplet
		135	1.35	Unknown
100	1.67	150	1.50	-CH <sub>2</sub> -NF <sub>2</sub> triplet
		165	1.65	Unknown
		217	2.17	Unknown
		221	2.21	Unknown
		228	2.28	Unknown
138	2.30	230	2.30	-O-CH <sub>3</sub>

<sup>a/</sup> Chemical shifts may be referenced to internal tetramethylsilane by applying the equation:  $\delta_{TMS} = 5.67 \text{ ppm} - \delta \text{ CH}_2\text{Cl}_2$ .

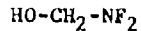
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assignment could not be verified in the  $^{19}\text{F}$  NMR spectrum of P-BEP because the absorption due to the fluorines of the side chain difluoramino group

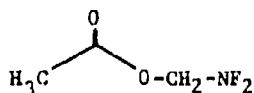


$J_{\text{H}-\text{F}} \approx 27 \text{ Hz}$  (Ref. 8)       $J_{\text{H}-\text{F}} = 23 \text{ Hz}$  (Ref. 9)

1



2



3

is a very broad signal completely devoid of fine structures. The broadness of this peak is the result of  $^{14}\text{N}$  quadrupole relaxation and the presence of numerous very similar but magnetically unequivalent side chain conformations.

(U) The only other strong absorption in the  $^1\text{H}$  spectrum of P-BEP is the sharp singlet at 2.30 ppm. This is assigned to the methyl group hydrogens of the  $-\text{CH}_2-\text{O}-\text{CH}_3$  side chains. The assignment is based on the sharpness of the signal and its position in the spectrum.

(U) All other absorptions in the  $^1\text{H}$  NMR spectrum of P-BEP are weak and are unidentified. Clearly these are due to end group structures and variations in main chain structures which very likely are related to variations in performance characteristics.

(C) The  $^1\text{H}$  NMR spectrum of P-BEP was also observed in acetonitrile- $d_3$ , acetic acid- $d_4$ , nitrobenzene and pyridine. It appears reasonably stable in acetone, acetonitrile, and nitrobenzene at 25°. In acetic acid some evolution of HF was observed after standing for several weeks. An immediate reaction is observed in pyridine.

(C) Figure VI-2 shows the 100 MHz  $^1\text{H}$  NMR spectrum of P-BEP in nitrobenzene (39 mg/0.5 ml). This spectrum did not change over a 3-month period at 25°C.

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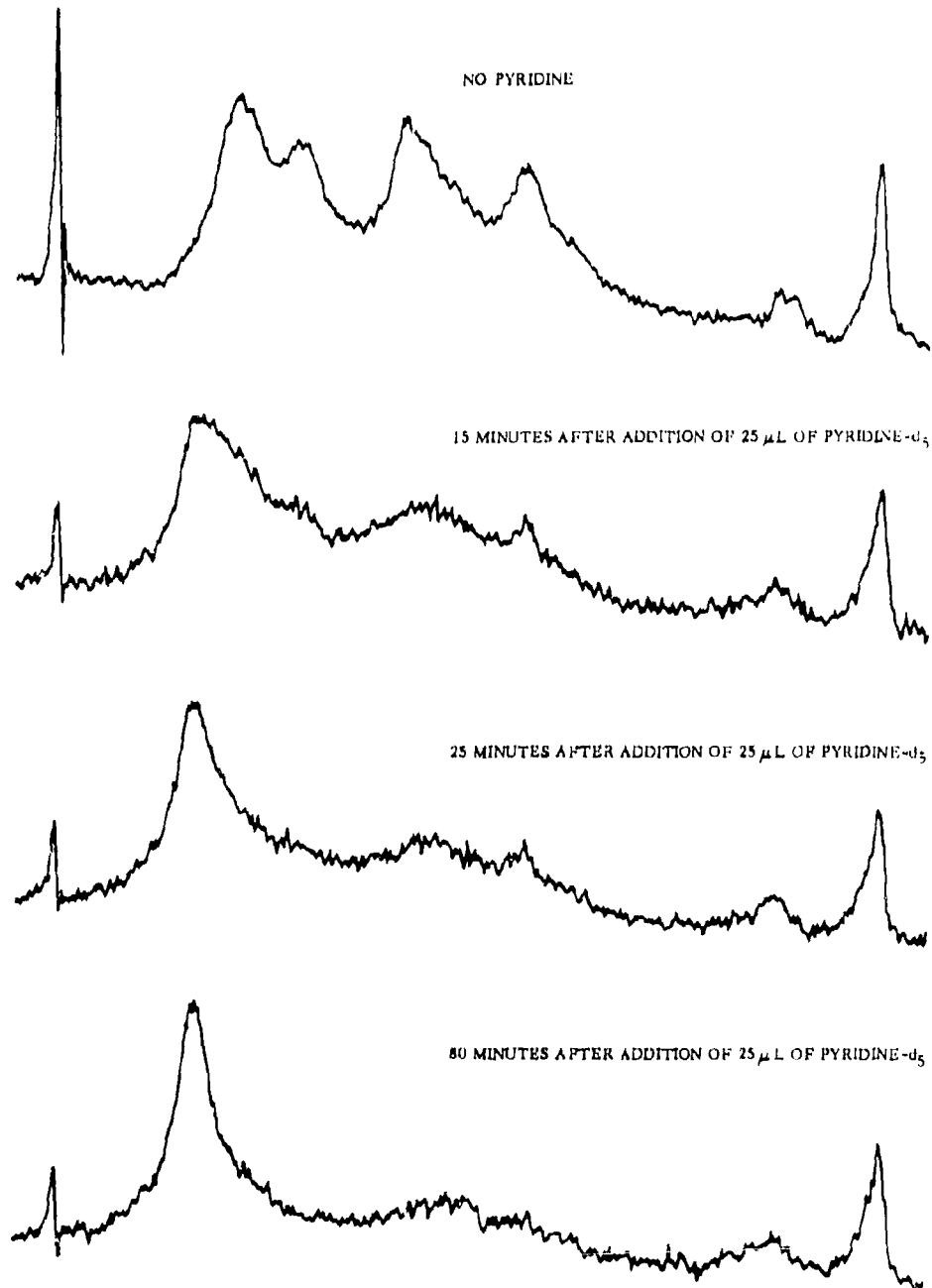


Figure VI-2 -  $^1\text{H}$  NMR Spectra of P-BEP in Nitrobenzene

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Figure VI-2 also shows the  $^1\text{H}$  spectral changes which occur with time upon addition of 25  $\mu\text{l}$ . of pyridine-d<sub>5</sub> (0.025 mg. - 0.06% by weight) to the nitrobenzene solution. After the addition of pyridine, the absorption assigned to the methylene hydrogens of the side chain difluoramino groups disappears rapidly. Since elimination of HF from these side chains is expected, this experiment confirms the assignment of the absorptions centered at 1.22 ppm to the methylene hydrogens of the side chains.

## 2. P-BEP stability:

(U) a. Mass spectrometry: The evolution of gaseous decomposition products from P-BEP was studied by mass spectrometry, infrared spectroscopy and gas chromatography. Chemical changes within the P-BEP polymer were investigated by infrared and ESR spectroscopy.

(U) The results of a brief study of the initial decomposition products observed from neat P-BEP utilizing the solid sampling (direct inlet) technique afforded many interesting insights into the mechanism of the thermal dissociation. A tabulation of the observed mass peaks resulting from the P-BEP degradation and the assigned ions is shown in Table VI-II. The temperature range for the study was from ambient to 140°C.

TABLE VI-II  
PRINCIPAL ION PEAKS OBSERVED DURING P-BEP DEGRADATION

m/e	Ions	m/e	Ions
20	HF <sup>+</sup>	31	CF <sup>+</sup> , CH <sub>3</sub> O <sup>+</sup>
26	CN <sup>+</sup>	33	NF <sup>+</sup>
27	HCN <sup>+</sup>	43	C <sub>2</sub> H <sub>3</sub> O <sup>+</sup>
28	N <sub>2</sub> <sup>+</sup> , CO <sup>+</sup> , C <sub>2</sub> H <sub>4</sub> <sup>+</sup>	44	CO <sub>2</sub> <sup>+</sup> , N <sub>2</sub> O <sup>+</sup>
29	CHO <sup>+</sup> , C <sub>2</sub> H <sub>5</sub> <sup>+</sup>	45	C <sub>2</sub> H <sub>5</sub> O <sup>+</sup>
30	NO <sup>+</sup>	52	NF <sub>2</sub> <sup>+</sup>
		53	HNF <sub>2</sub> <sup>+</sup>

(C) Other ions can be assigned to some of the m/e values; however, those shown represent the ions which are thought to be the major contributors to the particular mass value. In addition to the m/e values above, additional values were observed at m/e 47, 66, 82, and 101. These ions are thought to be arising from the fragmentation of Freon-11 which was used in the purification process. Workers at Dow (ref. 6) also studied the dissociation of P-BEP by the solid sampling technique. Their studies were conducted at 150°C, and the ion fragments were the same as observed in this

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study except for m/e 71 and 131. These fragments were not observed in the present study and m/e 85 ( $\text{SiF}_3^+$ ) was not observed in appreciable quantities at temperatures below 120°C. Figures VI-3 to VI-5 show the variation in peak intensity as a function of temperature for a number of the species resulting from the P-BEP decomposition. No correction could be made for a background contribution. In most cases, the initial peak intensity (at ambient temperature) is sufficiently small that it does not interfere with the interpretation of the observed curve.

(C) Hydrogen fluoride, the major species from the degradation, has been found to be present in P-BEP at room temperature. A mass spectrum obtained immediately after insertion of the sample probe shows an intense peak at m/e 20 ( $\text{HF}^+$ ). This peak rapidly decreases in intensity as the sample is allowed to remain at the ambient temperature in the mass spectrometer and reaches a constant peak height of rather low intensity. With increasing temperature, the evolution of HF proceeds rather slowly up to approximately 70°C. In this region, the evolution becomes more pronounced and the rate increases with temperatures up to 110°C. In the temperature region from 110-115°C, the production of HF increases very rapidly, and increasing the temperature from 115°C to 135°C results in an increase in the mass 20 peak from ~ 100 to 300 scale units.

(C) Hydrogen cyanide formation as a function of temperature parallels that of HF, although HCN is generated in smaller quantities. A mass spectrum obtained immediately after insertion of the probe does not show a large parent peak as is the case with HF, indicating that HCN is not present in the polymeric material as a dissolved gas. Hydrogen fluoride is formed at room temperature and is retained as a dissolved gas. This apparently is not the case with HCN. However, there is IR evidence that HCN is evolved at ambient temperature. Increasing the temperature from ambient to ~ 100°C results in a slow increase in HCN formation. Above this temperature the evolution of HCN becomes much more rapid but the increase is much less severe than in the case of HF. It is significant that the temperature range where HCN production begins to increase is the same temperature range where the evolution of HF becomes rapid.

(U) The production of  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ , and possibly NO can be observed by a comparison of m/e 44 and m/e 30 values as a function of temperature. Both curves remain almost constant up to ~ 75°C where m/e 44 shows an increase in the production of either  $\text{CO}_2$  or  $\text{N}_2\text{O}$ . The m/e 30 curve increases very slowly up to 90-100°C where the rate of evolution begins to increase. Both of these mass values were present immediately after insertion of the sample probe, with ion intensities greater than would be expected from air, indicating that these species may be present as dissolved gases in the P-BEP or are being slowly produced at room temperature.

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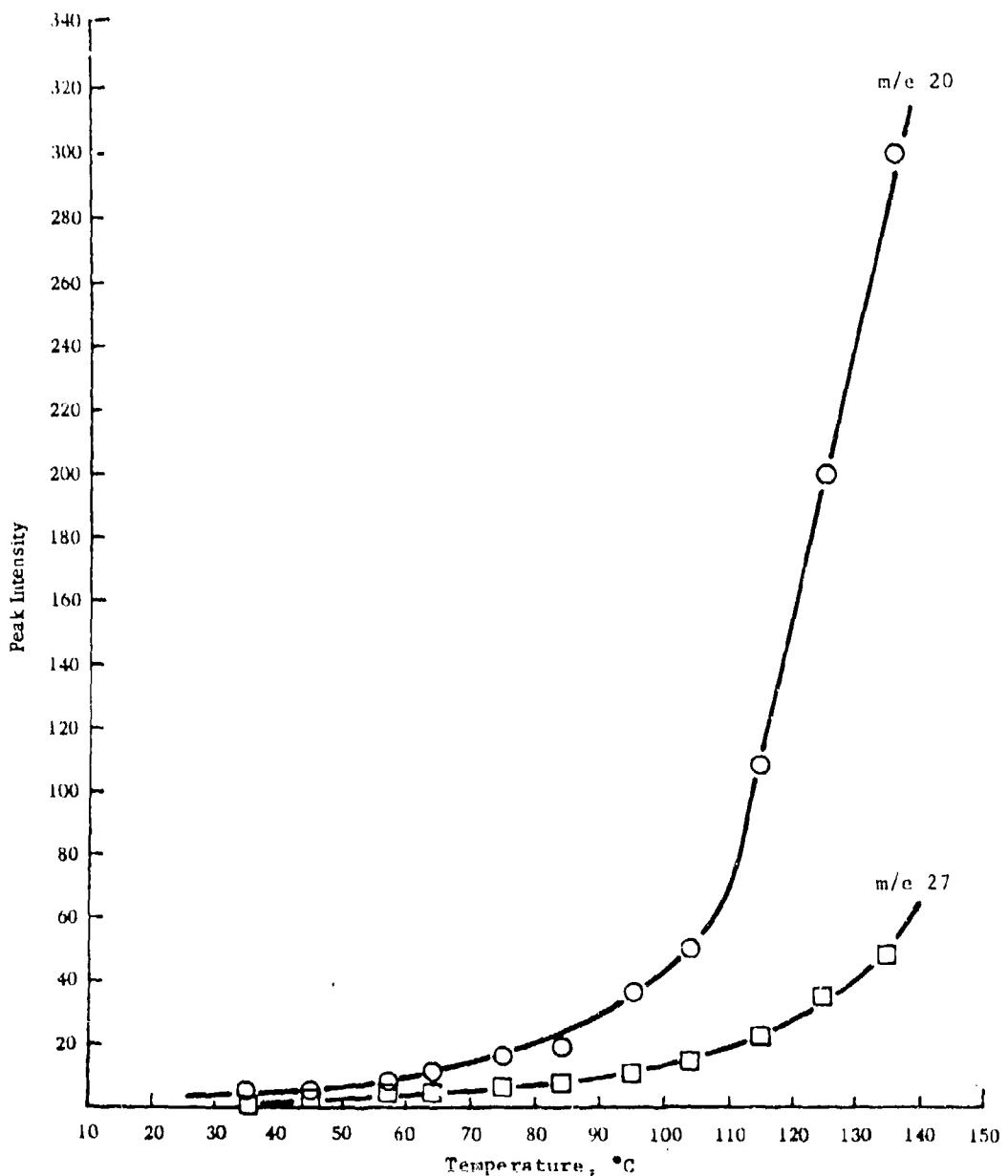


Figure VI-3 - Variation in Peak Intensity (arbitrary units) With Temperature for m/e 20 and 27

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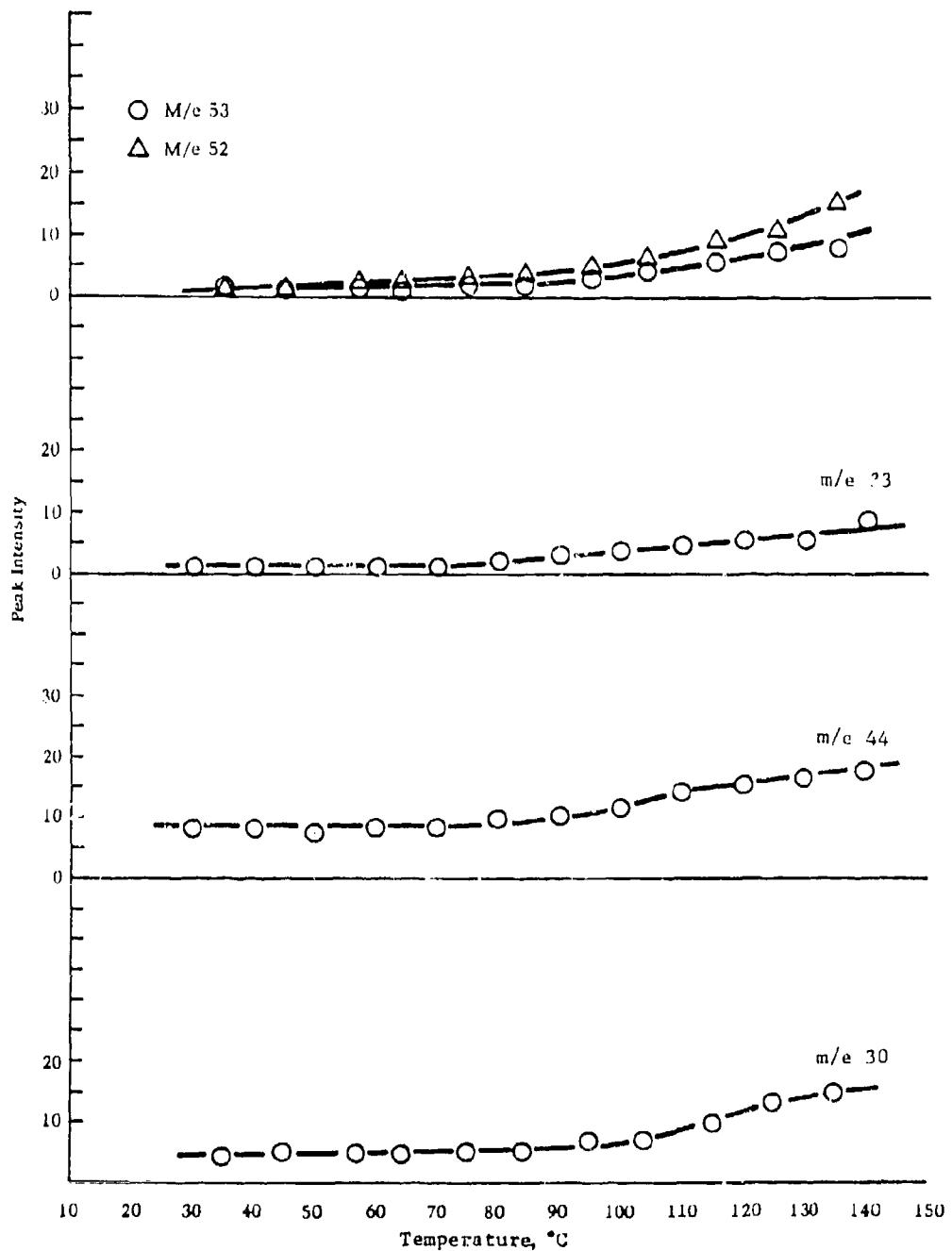


Figure VI-4 - Variation in Peak Intensity (arbitrary units) With Temperature

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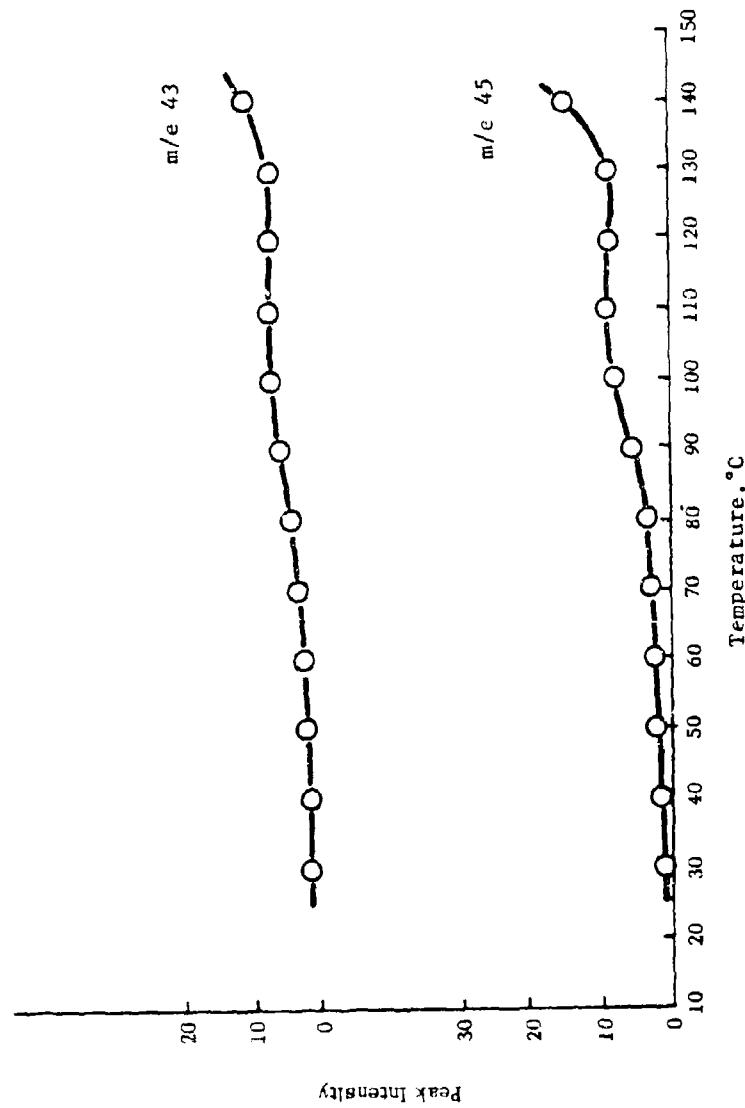


Figure VI-5 - Variation in Peak Intensity (arbitrary units) With Temperature For  $m/e\ 43$  and  $45$

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(C) Evolution of difluoramine, as evidenced by the curve for m/e 53, occurs very slowly up to 85°C. Above this temperature, the rate of production becomes much more pronounced. The curves for m/e 33 and m/e 52 both remain essentially constant up to 75-80°C, at which point the rate increases for both curves with the curve for m/e 53 increasing at a somewhat greater rate. The mass values 52 and 33 correspond to the  $\text{NF}_2^+$  and  $\text{NF}^+$  ions, respectively, and are the principal ions produced in the mass spectrum of tetrafluorohydrazine ( $\text{N}_2\text{F}_4$ ). Nitrogen trifluoride ( $\text{NF}_3$ ) also shows large relative abundances at m/e 33 and 52, in addition to the parent peak at m/e 71. In fact, the  $\text{NF}_2^+$  ion is the largest peak in the mass spectrum of  $\text{NF}_3$ , with the  $\text{NF}^+$  ion having a relative abundance of ~40. The Dow Ref. 6 Group has reported that the mass 53 peak consists of a doublet of equal intensity. The fragments observed at this mass value correspond to  $\text{HNF}_2^+$  and  $\text{HC}_2\text{N}_2^+$ .

(U) Mass 45 is probably due to the  $\text{C}_2\text{H}_5\text{O}^+$  ion and likely is formed as a result of the degradation of the terminal groups. The ion intensity increases very slowly up to 75-80°C, whereupon an acceleration of the rate is observed up to approximately 100°C. At this point, the rate appears to remain constant up to 130°C, and then increases much more rapidly at temperatures above 130°C.

(C) An interesting observation was made with the peaks at m/e 31 and 47. These two mass values correspond to  $\text{CF}^+$  for the former and to a number of ions, including  $\text{CCl}^+$ ,  $\text{COF}^+$  and  $\text{CH}_2\text{NF}^+$ , for the latter. Originally it was thought that the ion fragments at these mass values resulted from the fragmentation of Freon-11 and indeed the intensity vs. temperature curves do show an increase from room temperature to a maximum at approximately 75°C and then a decrease. This corresponds directly to the curve obtained for m/e 101, the  $\text{CCl}_2\text{F}^+$  fragment from the Freon. However, at approximately 110°C the ion intensity began to increase and showed a continual increase to 140°C. It is apparent that another process, resulting in the formation of ion fragments at m/e 47 and 31, is of importance at these higher temperatures. Such a process could involve the formation of the  $\text{COF}^+$  and  $\text{CF}^+$  ions.

(C) A plot of  $\log$  (ion intensity) as a function of  $\frac{1}{T}$  for m/e 20 and m/e 27 is shown in Figure VI-6. The data for m/e 20 give a relatively straight line at lower temperatures which can be extrapolated to cross the temperature axis at ~ 5°C. However, the plot for m/e 27 does not produce a straight line relationship and apparently shows a complex situation at lower temperatures. Due to the measurement of ions of very low intensity, considerable error may be expected in the data at lower temperatures. The data indicate, however, that HCN is evolved at temperatures less than ambient and that HF is evolved at or slightly above 5°C.

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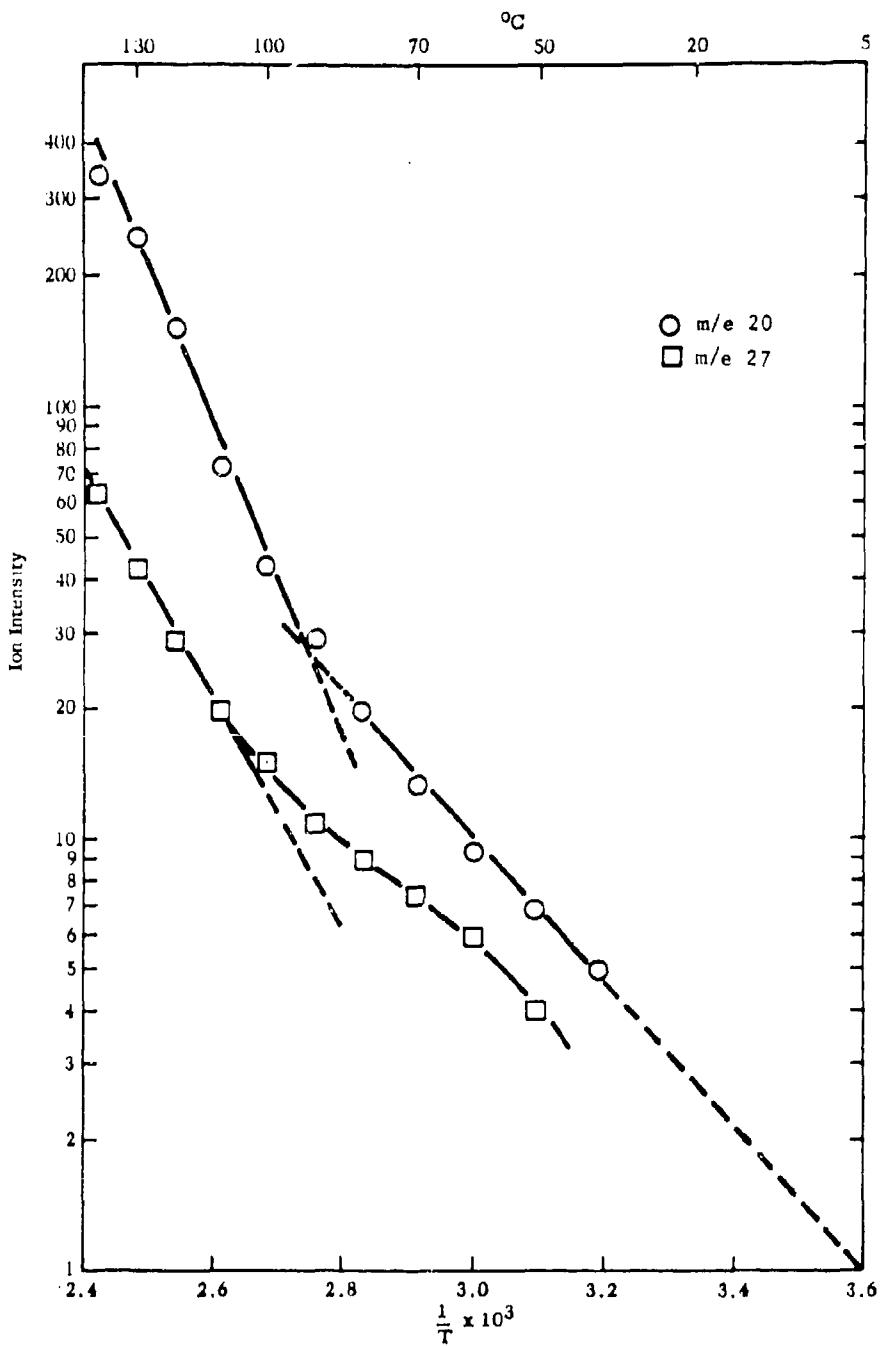


Figure VI-6 - Log (ion intensity) vs.  $1/T$  ("K)  
for  $m/e 20$  and 27

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(C) In general, the data show that P-BEP undergoes only slow degradation at temperatures lower than 70-80°C. However, HF begins to evolve at temperatures below ambient, HCN may be evolved at room temperature or slightly above and  $\text{HNF}_2$  some 10-20°C above ambient temperature. At temperatures above 80°C, considerable dissociation commences and above 120-130°C the rate of decomposition is quite rapid, as evidenced by the large relative increases in ion intensities.

(U) b. Thermal stability studies: Infrared spectroscopy was used extensively in studying the stability of P-BEP. Most of the work was concerned with P-BEP decomposition as a function of temperature for short term periods (16 hr.). In those studies, P-BEP was placed in a metal tube attached to a Kel-F infrared cell (Figure IV-2). The tube was heated to a constant temperature and the spectra were continuously recorded overnight.

(C) Products evolved from the heated P-BEP which were detected by IR were usually  $\text{CH}_2\text{Cl}_2$ , HF,  $\text{HNF}_2$ , HCN,  $\text{N}_2\text{O}$  and  $\text{CO}_2$ . The amounts of these materials reported in milliliters of standard gas per gram of P-BEP are presented in Table VI-III. The studies were conducted in different metal tubes. From Table VI-III, it appears that the smallest quantities of gaseous products are evolved in a copper reactor. However, extensive reaction of P-BEP and copper was noted; thus we believe that the volatiles probably reacted out before they could be detected. Monel, nickel, and stainless steel were then used. P-BEP did not appear to react with any of these. After preliminary studies in these metals, stainless steel was chosen for use in the detailed work. This choice was dictated on the grounds of convenience, since all of the metals except copper appeared to be compatible with P-BEP.

(U) Difficulty was experienced in getting reproducible results in the infrared studies. Runs made with the same quantities of P-BEP at the same temperature and monitored over the same time periods gave a scatter of points. However, the effect of temperature and time is critical enough that the data spread at a particular temperature was not sufficient to affect the conclusions drawn from these studies. The variance in data gathered from identical runs appears to depend to a very large extent upon the quantities of residual  $\text{CH}_2\text{Cl}_2$  in the P-BEP itself.

(U) The overnight runs generated volatile products at temperatures between 50°C and 120°C. In these runs, the volatile products were usually evolved within the first 2 hr. and remained essentially constant during the remaining time. The first species detected was  $\text{CH}_2\text{Cl}_2$ . Methylene chloride is tenaciously held by P-BEP and cannot be completely removed, even after several days of continuous pumping at  $10^{-4}$  mm. The methylene chloride content of various samples does not appear to be related to how long the sample is pumped. In some cases, samples pumped for 2 hr. yielded about

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TABLE VI-III

P-BEP DECOMPOSITION PRODUCTS IDENTIFIED BY  
INFRARED ANALYSIS

	<u>Time</u> <u>(days)</u>	<u>T</u> <u>(°C)</u>	<u>CH<sub>2</sub>Cl<sub>2</sub></u> <u>(ml/g)</u>	<u>HF</u> <u>(ml/g)</u>	<u>HNF<sub>2</sub></u> <u>(ml/g)</u>	<u>HCN</u> <u>(ml/g)</u>	<u>N<sub>2</sub>O</u> <u>(ml/g)</u>	<u>Remarks</u>
Copper	7	25	1.7	-	-	-	-	
	19	25	-	-	-	-	-	
	0.7	60	1.6	-	-	-	-	
	0.7	77	2.0	-	-	0.2	-	
	0.7	80	1.4	3	0.02	0.8	0.5	
	0.7	80	3.0	9	0.02	1.0	1.3	
	0.7	100	0.8	4	0.20	0.8	0.1	
	0.7	110	1.7	12	-	0.7	1.0	
	0.7	120	2.1	23	-	0.3	0.8	
	0.3	130	0.8	7	0.02	1.1	0.6	
Monel	0.7	100	2.6	26	0.16	2.4	1.1	
	0.7	100	2.6	34	0.40	3.3	3.0	
	0.7	112	1.6	32	0.06	1.8	0.8	
Ni	0.7	100	2.2	29	0.10	2.7	0.7	
Stainless Steel	1	40	2.8	-	-	-	-	
	4	40	2.8	-	-	-	-	
	6	40	2.4	-	-	-	-	
	0.7	50	0.4	-	-	-	-	
	1	55	2.8	-	-	-	-	
	4	55	3.0	tr*	0.01	0.3	0.2	
	6	55	2.8	-	0.01	0.7	0.8	
	0.7	60	2.3	-	0.03	0.4	-	
	0.7	60	2.7	1	0.03	0.8	-	
	0.7	60	0.7	-	-	0.1	-	
	0.7	70	5	1	0.04	1.7	-	NF <sub>3</sub> (tr)
	4	70	3.0	1	0.02	1.5	0.6	
	6	70	3.0	1	-	0.7	2.1	
	0.7	80	1.6	1	0.40	0.4	0.1	
	0.7	80	2.1	1	0.02	0.9	1.0	
	0.7	80	1.5	2	-	0.8	1.1	
	0.7	80	2.3	1	-	0.6	0.8	
	0.7	100	2.3	12	0.04	2.6	0.8	
	0.7	100	1.9	23	0.10	2.2	0.8	
	0.7	100	2.7	40	0.30	4.3	1.4	
	0.7	100	1.9	11	0.10	2.4	0.2	

\* Trace quantities.

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1.0 to 1.5 ml.  $\text{CH}_2\text{Cl}_2$  per gram of P-BEP, while samples pumped for several days yielded 2.5 to 3.0 ml. gas.

(C) After  $\text{CH}_2\text{Cl}_2$  has been liberated, three primary volatile decomposition products from P-BEP are observed. These products are HF, HCN, and  $\text{HNF}_2$ . They all appear nearly simultaneously within the first few scans depending upon the temperature of the run. With increasing temperature, products were evolved more quickly and in greater concentration. However, even at the low temperatures and times, trace quantities may have been present.

(C) Infrared is not particularly sensitive to very small quantities of material. Our calibrations indicate the following limits of detection: HF - 1 ml/g; HCN - 0.1 ml/g;  $\text{HNF}_2$  - 0.01 ml/g;  $\text{N}_2\text{O}$  - 0.1 ml/g; and  $\text{CH}_2\text{Cl}_2$  - 0.1 ml/g. These IR analyses were supplemented by GC and mass spectrometry which are somewhat more sensitive than infrared.

(C) Preliminary studies have indicated that HCN and  $\text{HNF}_2$  are generated from P-BEP in glass at ambient temperatures. The HF generated was found in very substantial quantities as  $\text{SiF}_4$  which should be expected. It is not surprising that HCN is observed since many organo nitriles will liberate HCN at room temperature. It does indicate, however, that the P-BEP polymer does contain some nitrile functionalities.

(C) The fact that HF,  $\text{HNF}_2$ , and HCN are observed indicates that decomposition occurs through radicals F,  $\text{NF}_2$ , and CN. These radicals apparently abstract available H atoms from the polymer before they have a chance to react with themselves to form halogen or pseudo-halogen type molecules.

(C) The stable decomposition products,  $\text{CO}_2$  and  $\text{N}_2\text{O}$ , are for most cases insignificant in the 16-hr. studies. These materials appear in large quantity only if substantial amounts of the primary products (HF,  $\text{HNF}_2$ , and HCN) are present.

(C) The amounts of gas evolved do not affect substantially the infrared spectrum of P-BEP residue. In most of the runs reported in Table VI-III smears of P-BEP residue were spread on AgCl plates and the infrared spectra recorded. In every case, no major change was detected in the solid residue when compared to a similar sample of unheated P-BEP. For example, no increases in the C≡N functionality or in the C=O functionality were detected. This observation leads us to believe that elimination of F,  $\text{NF}_2$ , and CN to form HF,  $\text{HNF}_2$ , and HCN is probably due to random extraction of hydrogen from the polymer.

(C) From the amounts of these primary products, it would appear that the most abundant decomposition radical is F; the next most abundant would

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be CN which forms HCN, and finally NF<sub>2</sub> which yields HNF<sub>2</sub>. The evolution of HF, HCN, and HNF<sub>2</sub> is very rapid within the first few hours when heating P-BEP at a constant temperature. After these products are evolved the rate of evolution falls off rapidly and nearly ceases below 80°C. Above 80°C the same is noted except that the rate of product evolution does not fall off as much. We interpret this observation to mean that the lower molecular weight fractions of P-BEP (which are generally assumed to be less stable than the higher fractions) are responsible for the degradation products noted in the infrared spectra. After these low-weight fractions are decomposed, degradation of the more stable, more abundant higher weight fractions occurs at a very much slower rate at any given temperature.

(C) In addition to the overnight runs in which the volatilization of products was followed, a series of runs were made in which P-BEP polymer was heated and its spectrum recorded continuously overnight (16 hr.). The spectra show that little internal change occurred in the P-BEP over the temperature range studied (60°C to 140°C). This lack of change is in accord with the interpretation that the low molecular fragments of the P-BEP polymer decompose first. Early runs at 200°C indicated that pronounced changes occurred at elevated temperatures where -C=N functionalities readily appeared within a few hours.

(U) A gas chromatographic (G.C.) analysis was made of gaseous products evolved in the overnight (16 hr.) P-BEP stability studies and on all the longer term investigations. The technique enabled the identification and quantitative analysis of N<sub>2</sub>, O<sub>2</sub>, CO, NO, CO<sub>2</sub>, and N<sub>2</sub>O evolved as P-BEP decomposition products. The limit of sensitivity to the first four gases was approximately 0.02 ml. of gas/g of P-BEP while the CO<sub>2</sub> and N<sub>2</sub>O could be quantized to 0.1 ml/g of P-BEP.

(U) Little gaseous decomposition was detected by G.C. in 16 hr. below 70°C. At 70°C only trace quantities of N<sub>2</sub>, CO, NO, and CO<sub>2</sub> were detected. After longer time intervals decomposition products could be detected at lower temperatures. Table VI-IV shows the results of a number of the G.C. analyses. The quantities of decomposition products detected at 40, 55, and 70° after 6 days are shown in Figure VI-7.

(C) c. Sealed tube studies: Samples of the P-BEP were placed in stainless steel tubes which had been passivated with ClF<sub>3</sub>, evacuated at 10<sup>-5</sup> Torr for 2 hr. to remove excess solvent, and sealed. The samples were placed in 25, 40, 55 and 70°C constant temperature bath and removed after 30 days for analysis for gaseous decomposition products by gas chromatography, infrared spectroscopy, and mass spectrometry. Table VI-V shows the results of the gas phase analysis of these samples. These results substantiate the conclusion that P-BEP decomposes at a significant rate even at 40°C.

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TABLE VI-IV

GAS CHROMATOGRAPHIC ANALYSES OF P-BEP DECOMPOSITION PRODUCTS

Time (days)	Temp. (°C)	Gaseous Product (ml/g of P-BEP)				
		N <sub>2</sub>	CO	NO	CO <sub>2</sub>	N <sub>2</sub> O
0.7	70	-	-	(t)*	(t)	-
0.7	80	0.3	0.1	0.04	0.2	0.2
0.7	100	0.3	0.1	-	0.2	(t)
1	40	-	-	-	-	-
1	55	-	-	-	-	-
4	40	0.1	-	-	(t)	-
4	55	0.2	0.05	-	(t)	-
4	70	0.5	0.2	-	0.2	(t)
6	40	-	-	-	(t)	-
6	55	0.5	0.1	-	0.5	0.3
6	70	1.6	0.5	-	1.7	0.8

\* Trace quantities are denoted by (t).

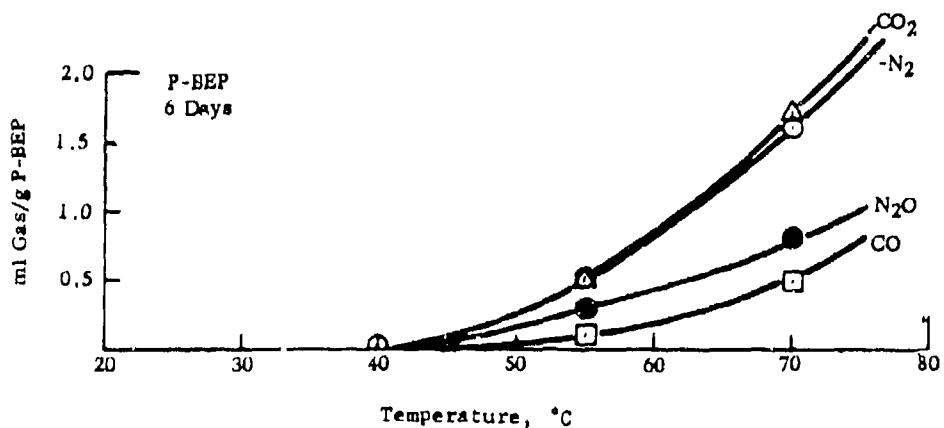


Figure VI-7 - Gaseous Products from P-BEP as a Function of Temperature

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TABLE VI-V

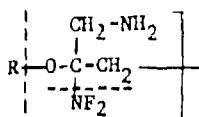
GASEOUS PRODUCTS OF P-BEP DECOMPOSITION

Time (days)	Temp. (°C)	Gaseous Products (ml/g of P-BEP)								
		N <sub>2</sub>	CO	H <sub>2</sub>	CO <sub>2</sub>	N <sub>2</sub> O	CH <sub>4</sub>	HF	HCN	CH <sub>2</sub> Cl <sub>2</sub>
31	25	-	-	-	-	-	-	-	-	2.1
31	40	7.5	0.7	-	0.2	0.1	-	1.0	1.5	2.5
35	55	5.4	0.9	-	0.4	0.1	-	2.0	2.6	2.8
35	70	3.5	2.3	(tr)	1.1	0.1	(tr)	6.5	0.7	2.8

(U) d. Electron spin resonance: Electron spin resonance (ESR) studies were made to ascertain whether P-BEP contained residual paramagnetic species or whether such species could be detected during its thermal decomposition. An evacuated sample (40 - 50 mg.) was placed in the variable temperature assembly and spectra were obtained at temperatures from 25° to 175°C. No absorption peak was observed from 25° to 130°C. At 130°C a peak began to appear and increased in intensity with increasing temperature to 170°C. This is the same temperature region where changes could begin to be noted by infrared. Additional studies of the neat material at temperatures up to 200°C produced a moderate increase in the signal level, but no additional fine structure was resolved. Rapid cooling of the sample to -150°C did not improve the fine structure.

(U) Using the Varian computer of average transients (CAT) accessory, a time-average spectrum of 36 1-min. scans was obtained. It was of sufficient detail and intensity to show the observed signal to be a singlet having a g-value very close to 2.001 (Figure VI-8).

(C) The signal was sufficiently narrow that N, F or H splitting should have been resolved, were it present. Based on the assumption that the unpaired electron was located on an atom not bonded to any of the above three nuclei, only two bond cleavages could lead to such a radical. They are:



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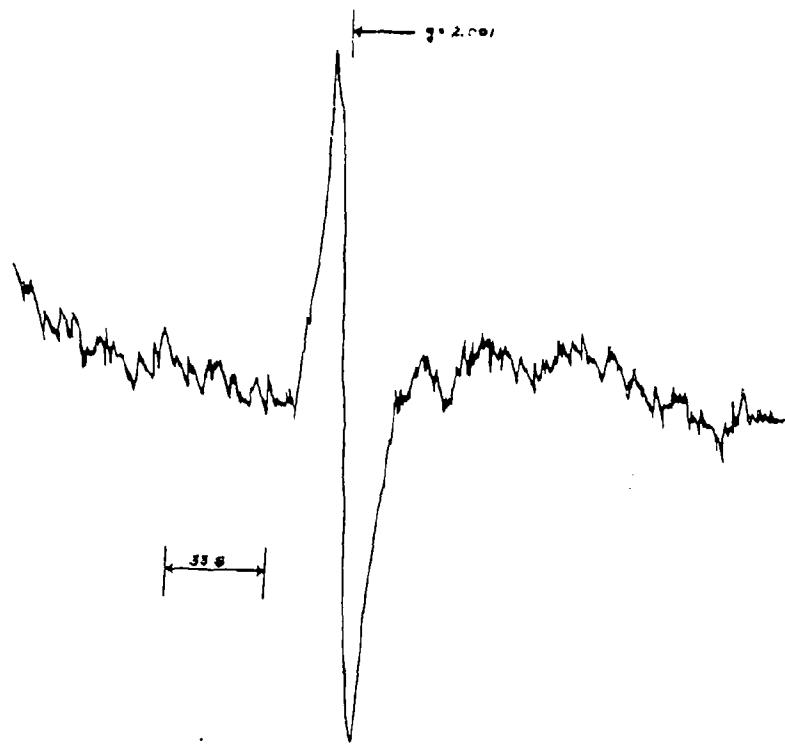


Figure VI-8 - Time Average EPR Spectrum of P-BEP  
Absorption Peak

(C) If a C-O bond cleavage were to occur, it would more likely occur adjacent to the tertiary carbon atom. As a consequence, it is likely that the signal is due to cleavage of the NF<sub>2</sub> group from the tertiary carbon. It is not surprising that the companion NF<sub>2</sub> radical is not observed since it cannot be detected by EPR in N<sub>2</sub>F<sub>4</sub> under conditions where it is known to be present in appreciable concentrations.

(C) e. Nuclear magnetic resonance: Nuclear magnetic resonance (NMR) studies were undertaken to determine if detectable changes in P-BEP occurred within the framework of temperatures previously discussed. Because of instrument temperature limitations and solvent volatility, NMR studies were restricted below 130°C. No significant changes in the <sup>19</sup>F or <sup>1</sup>H NMR spectra were noted. These observations substantiate IR studies of the solids as a function of temperature.

(C) 3. P-BEP/oxidizer compatibility: Both short term and extended studies on the compatibility of P-BEP with the oxidizers HAP, HP-2, DOAP, and AP were conducted. Continuous infrared monitoring of gas evolution was

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conducted as a function of time and temperature; at the conclusion of these experiments the gaseous products were also analyzed by gas chromatography to quantitatively determine those gases not sensitive to IR analysis. Direct inlet mass spectrometer was used to study P-BEP/oxidizer interactions as a function of temperature. Longer term (up to 3 month) sealed tube studies were conducted on P-BEP oxidizer mixtures.

(C) a. Short-term thermal studies. Gaseous decomposition products evolved from P-BEP/oxidizer mixtures were investigated by infrared spectroscopy, gas chromatography and mass spectrometry. The primary objective was to determine the compatibility of HAP and HP-2 with P-BEP. Studies with AP were included for reference purposes.

(C) P-BEP/oxidizer systems were studied in the same manner as pure P-BEP. A 2:1 weight ratio of P-BEP to oxidizer was used in these studies (100 to 50 mg., respectively). The infrared data are presented in Table VI-VI. The numbers are reported in milliliters of gas evolved per gram of P-BEP.

(C) The infrared data indicate that considerably larger quantities of degradation products are noted in the P-BEP/HAP and P-BEP/HP-2 systems than from P-BEP alone. The P-BEP/AP system differs little from pure P-BEP.

(C) Continuous generation of volatile decomposition products is noted, in contrast to neat P-BEP where products were evolved early to a near steady state value. We also observed  $N_2F_4$  and  $NF_3$  occasionally as P-BEP decomposition products when HAP and HP-2 were present. The evolution of  $N_2F_4$  and  $NF_3$  appears to relate to  $HNF_2$ , since  $HNF_2$  occasionally disappears in the 16-hr. runs accompanied by increases in the quantities of  $N_2F_4$ .

(C) Another interesting observation is that  $CH_2Cl_2$  reacts out of the system. In all of the long-term studies, methylene chloride content in the gas phase decreased substantially. At 55° and 70°C all  $CH_2Cl_2$  is virtually reacted out in 4 days. In pure P-BEP the long-term studies did not indicate so marked a decrease nor is it noted in P-BEP/AP systems.

(C) Methyl formate ( $HCO_2CH_3$ ) was also evolved sporadically. The presence of this compound is unexplained, as it is not a logical decomposition product of P-BEP/oxidizer systems. Since it was noted after long time periods, it may be related to the disappearance of  $CH_2Cl_2$ .

(C) Gas chromatographic analysis of the gaseous products showed that HP-2 was the most reactive of the three oxidizers with P-BEP. Significant amounts of reaction could be detected at 50°C in 16 hr. Gaseous products detected by G.C. at this temperature included  $N_2$ , CO, NO,  $CO_2$  and  $N_2O$ . In

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TABLE VI-VI

VOLATILE DECOMPOSITION PRODUCTS AS DETERMINED BY INFRARED  
IN P-BEP/OXIDIZER SYSTEMS AS A FUNCTION  
OF TEMPERATURE AND TIME

Oxidizer	Time (days)	T (°C)	CH <sub>2</sub> Cl <sub>2</sub> (ml/l)	HF (ml/l)	HNF <sub>2</sub> (ml/l)	HCN (ml/l)	N <sub>2</sub> O (ml/l)	Others
HAP	7	25	1.4	-	-	-	-	-
	14	25	1.5	-	-	-	-	-
	18	25	0.8	-	-	-	-	-
	7	40	1.3	-	-	-	-	-
	16	40	1.6	tr*	0.3	1.5	-	-
	21	40	0.4	-	-	1.1	2.1	-
	0.7	55	2.7	-	-	-	-	-
	0.7	55	2.5	tr	0.18	1.8	tr	N <sub>2</sub> F <sub>4</sub> (0.1)
	7	55	1.5	-	-	1.1	-	N <sub>2</sub> F <sub>4</sub> (2)
	16	55	-	2	0.02	-	-	N <sub>2</sub> F <sub>4</sub> (3)
	21	55	-	2	-	1.5	-	N <sub>2</sub> F <sub>4</sub> (2)
	0.7	65	2.1	-	0.14	-	-	N <sub>2</sub> F <sub>4</sub> (0.1)
	0.7	65	2.1	9	0.23	2.5	1.5	N <sub>2</sub> F <sub>4</sub> (0.1)
	7	70	2.6	-	-	-	-	NF <sub>3</sub>
	14	70	-	2	-	-	21	HCO <sub>2</sub> CH <sub>3</sub>
	18	70	-	1	-	-	20	NF <sub>3</sub>
	0.7	80	2.6	16	0.52	4.2	4.0	N <sub>2</sub> F <sub>4</sub> (3)
	0.7	80	2.8	8	0.07	3.5	4.4	-
	0.7	80	0.6	7	0.01	2.5	6.0	-
	2.5	85	2.2	14	-	-	8.4	-
HP-2	4	25	2.2	-	0.01	0.3	0.2	-
	4	40	2.2	-	-	1.0	2.5	NF <sub>3</sub>
	0.7	50	2.2	-	tr	0.9	1.2	N <sub>2</sub> F <sub>4</sub> (tr)
	0.7	50	3.5	-	0.09	1.0	tr	-
	4	55	-	3	-	1.7	12.5	N <sub>2</sub> F <sub>4</sub> (4), NF <sub>3</sub> + HCO <sub>2</sub> CH <sub>3</sub>
	0.7	60	0.7	-	0.16	1.0	-	-
	0.7	60	2.5	-	0.14	2.9	1.4	N <sub>2</sub> F <sub>4</sub> (0.6)
	4	70	-	-	-	-	20	NF <sub>3</sub>
	0.7	80	3.0	8	0.53	4.7	3.0	N <sub>2</sub> F <sub>4</sub> (2)
	0.7	80	1.2	7	0.11	3.3	4.7	N <sub>2</sub> F <sub>4</sub> (0.2)
	0.7	80	2.3	7	0.19	3.1	2.2	N <sub>2</sub> F <sub>4</sub> (2)
	1	85	0.6	3	-	1.7	6.4	-
	4	85	-	15	-	0.6	30	NF <sub>3</sub>

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TABLE VI-VI (Concluded)

Oxidizer	Time (days)	T (°C)	CH <sub>2</sub> Cl <sub>2</sub> (ml/g)	HF (ml/g)	HNF <sub>2</sub> (ml/g)	HCN (ml/g)	N <sub>2</sub> O (ml/g)	Others
AP	6	40	2.4	-	-	-	tr	
	0.7	55	3.8	-	0.01	-	-	
	6	55	2.8	-	0.02	0.7	0.8	
	0.7	65	2.3	1	0.02	0.1	-	
	6	70	2.8	tr	-	2.0	1.0	
	0.7	80	4.0	2	0.05	0.8	tr	
	0.7	80	1.1	1	0.03	0.3	-	

\* Trace quantities.

longer-term studies the quantities of the gaseous products increased significantly even at 40°C. Large quantities of CO, CO<sub>2</sub>, and N<sub>2</sub>O were formed, indicating the oxidative degradation of P-BEP was occurring. It is not apparent whether N<sub>2</sub>O was being formed by the oxidation of the hydrazinium ion or by attack of the NF<sub>2</sub> substituents on P-BEP. Nitrogen is a major gaseous product from the P-BEP/HP-2 reaction. Studies on the thermal decomposition of HP-2 at MRI and at Reaction Motors Division of Thiokol Chemical Company (Ref. 10) showed N<sub>2</sub> as a decomposition product but no evidence for the formation of N<sub>2</sub>O. It appears, therefore, that N<sub>2</sub> formation is a measure of oxidizer degradation while the CO, CO<sub>2</sub>, and N<sub>2</sub>O are indicative of P-BEP degradation and/or oxidation. Figure VI-9 shows the quantities of gas evolved at 25, 40, 55 and 70°C in 4 days from a P-BEP/HP-2 mixture. By comparison the quantities of these gases evolved from P-BEP or HP-2 alone over this time period are two orders of magnitude smaller. For example, the total quantity of N<sub>2</sub>, CO, CO<sub>2</sub>, and N<sub>2</sub>O evolved from P-BEP in 4 days at 55°C is < 1 ml/g of P-BEP. At 70°C over the same time period < 0.1 ml. of gas/g is evolved from HP-2. This compares to over 100 ml. of gas evolved per gram of P-BEP or 200 ml/g of HP-2 evolved from the mixture at 70° in 4 days. At 40°C little decomposition of either P-BEP or HP-2 can be detected in 4 days while the mixture liberates > 13 ml. of gas per gram of P-BEP.

(C) The P-BEP/HAP mixture appeared to be less reactive than P-BEP/HP-2, particularly below 55°C. The gaseous products observed by G.C. were N<sub>2</sub>, CO, NO, CO<sub>2</sub>, and N<sub>2</sub>O. Nitric oxide was often observed in the 16-hr. studies but was seldom detected in longer term studies. Figure VI-10 shows the quantities of gas evolved from a P-BEP/HAP mixture in 7 and 18 days at 25, 40, 55 and 70°C.

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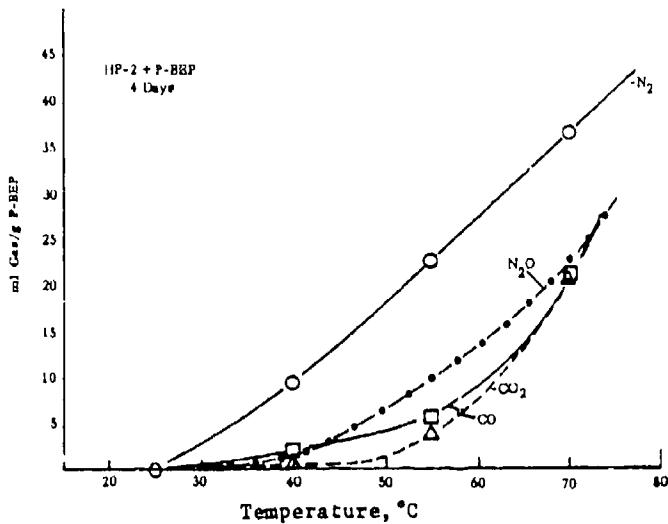


Figure VI-9 ~ P-BEP/HP-2 Decomposition Products Detected by Gas Chromatography After 4 Days

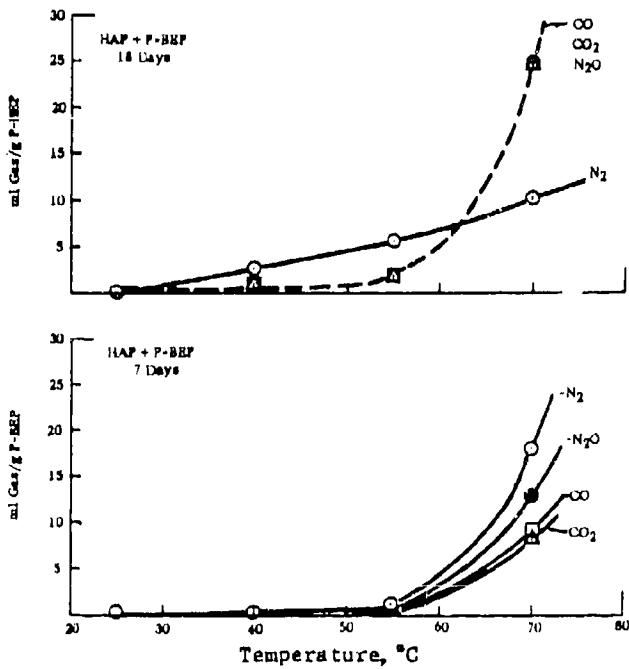


Figure VI-10 ~ P-BEP/HAP Decomposition Products Detected by Gas Chromatography After 7 and 17 Days

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(C) The 16-hr. studies showed little reaction at 55°C or lower temperatures. At 65°C and 80°C appreciable amounts of reaction were detected. The results of the 16-hr. studies indicate that HAP is slightly more reactive with P-BEP above 60°C than is HP-2; however, 4-day studies show the reverse to be true.

(C) HAP is reported to undergo a crystal phase change at 60°C (Ref. 11). Communications with personnel at NOS, Indian Head, Maryland, (Ref. 12) indicate that this change may instead be a dehydration of HAP. If HAP does dehydrate at 60°C, the water liberated could promote decomposition leaving the impression that HAP is more reactive than HP-2 above 60°C. In longer-term studies, however, the relative amount of product formation promoted by the water liberated would be small compared to the total amount of reaction products generated and thus HP-2 over more extended time periods might again prove to be more reactive. These results support this interpretation.

(C) The P-BEP/AP mixtures show little if any reaction beyond that expected for P-BEP alone. Figures VI-11 and VI-7 show the relative amounts of gaseous products generated by the P-BEP/AP mixture and P-BEP alone. These results indicate that, in fact, AP may have a stabilizing effect on P-BEP.

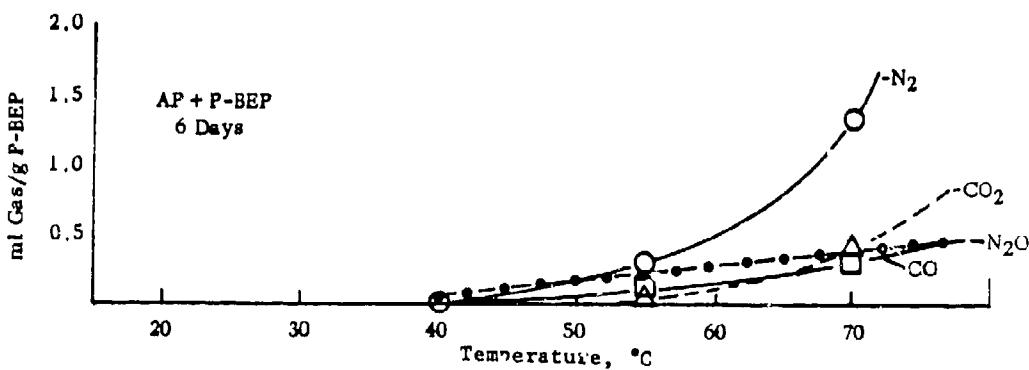


Figure VI-11 - P-BEP/AP Decomposition Product Detected by Gas Chromatography After 6 Days

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(C) b. Sealed tube studies: At an early stage of this program, it was determined that the prospects of obtaining a stable propellant containing both P-BEP and HP-2 were remote. As a consequence the longer term compatibility studies were conducted only with HAP and AP. Data accumulated in the sealed tube studies on the compatibility of P-BEP with HAP and AP are shown in Table VI-VII.

(C) The results of these longer terms studies of P-BEP/oxidizer compatibility show conclusively that P-BEP is substantially more compatible with AP than with HAP. There is little evidence that AP contributes to the decomposition or degradation of P-BEP at 60°C and below. The relatively short-term compatibility studies on P-BEP/HP-2 clearly shows the oxidative attack of P-BEP by HP-2 even at the lower temperatures.

(C) c. Mass spectrometry studies: Mass spectrometric studies, using the direct inlet technique, were conducted on mixtures of P-BEP with HAP and HP-2. The P-BEP was purified by the Freon-11 technique and all samples were prepared in a dry box with a dew point of -80°F. Each mixture was maintained under an inert atmosphere until the sample was degassed in the mass spectrometer. For the data at the ambient temperature of the mass spectrometer (~ 30°C), the first mass spectrum was obtained as soon as possible after the probe was in position; this time interval was approximately 5 to 7 sec. Additional spectra were obtained at various time intervals while the sample remained at the ambient temperature. When heating, the probe temperature was normally raised in 10°C intervals except in temperature regions of particular interest. At a given temperature, one mass spectrum was obtained as soon as the probe equilibrated at that temperature. After allowing the sample to remain at constant temperature for 4 to 5 min., a second spectrum was obtained and then the sample temperature raised to the next level.

(C) P-BEP/HAP: The major mass peaks resulting from the thermal degradation of a mixture of P-BEP and HAP are shown in Table VI-VIII. The temperature range for this study was from 30°C to 80°C.

(U) Other ions can be assigned to some m/e values; however, those shown represent the ions which are thought to be the major contributor to the particular mass value. In addition to the listed m/e values, other ions were observed at m/e 51, 83, and 100. As would be expected, these ions result from the ionization and fragmentation of perchloric acid.

(C) Figures VI-12 and VI-13 show the variation in peak intensity as a function of time (at 30°C) and temperature for a number of the species resulting from the decomposition of the mixture. No correction has been made for a background contribution. In most cases, however, the initial peak intensity is sufficiently small that it does not interfere with the interpretation of the observed curve. The major gaseous products resulting

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TABLE VI-VII  
GASEOUS PRODUCTS FROM P-BEP/OXIDIZER MIXTURES

Oxidizer	Time (days)	Temp. (°C)	Gaseous Products (ml. gas/kg of P-BEP)									
			H <sub>2</sub>	N <sub>2</sub>	CO	NO	CH <sub>4</sub>	CO <sub>2</sub>	N <sub>2</sub> O	SiF <sub>4</sub>	HCN	Other
AP	30	25	-	-	-	-	-	-	tr	-	-	CH <sub>2</sub> Cl <sub>2</sub>
	40	-	0.4	0.1	-	-	-	-	-	-	0.7	CH <sub>2</sub> Cl <sub>2</sub>
	55	-	0.6	0.2	-	-	1.1	0.3	-	-	-	CH <sub>2</sub> Cl <sub>2</sub> , HF (1.0)
	70	tr	2.1	4.9	-	tr	7.1	0.2	-	-	0.4	CH <sub>2</sub> Cl <sub>2</sub> , HF (1.5)
AP	50	25	-	-	-	-	-	-	-	2.8	-	-
	40	-	0.3	tr	-	-	-	-	-	-	0.8	-
	60	4.8	1.5	1.8	-	tr	0.8	-	-	-	1.5	CH <sub>2</sub> CH <sub>3</sub>
	80	11.6	8.1	14.7	-	tr	6.8	tr	-	-	-	-
AP	50	25	-	-	0.7	0.2	0.3	-	-	2.4	-	-
	40	-	5.4	4.5	3.6	-	tr	3.5	-	-	-	-
	60	13.3	4.5	14.7	-	tr	6.3	tr	-	-	3.3	CH <sub>2</sub> CH <sub>3</sub>
	80	-	-	-	-	-	-	-	-	-	-	-
AP	101	25	-	0.2	0.2	-	-	-	-	7.3	-	CH <sub>2</sub> Cl <sub>2</sub>
	40	-	0.6	0.2	-	-	-	-	-	-	1.5	CH <sub>2</sub> Cl <sub>2</sub>
	60	31.4	0.8	2.0	-	tr	0.8	-	-	1.0	-	CH <sub>2</sub> Cl <sub>2</sub>
	80	74.4	2.3	10.4	-	0.2	5.3	-	-	-	1.5	CH <sub>2</sub> Cl <sub>2</sub>
AP	101	25	-	-	-	-	-	-	-	6.0	0.1	Air
	40	-	0.2	0.2	-	-	-	-	-	-	1.7	CH <sub>2</sub> Cl <sub>2</sub>
	60	49.5	1.8	2.0	-	-	-	1.3	-	0.2	0.1	CH <sub>2</sub> Cl <sub>2</sub>
	80	46.2	2.5	5.0	-	3.3	3.0	-	-	-	-	CH <sub>2</sub> Cl <sub>2</sub>

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TABLE VI-VII (Concluded)

Oxidizer	Time (days)	Temp. (°C)	Gaseous Products (ml. gas/g. of P-BEP)							
			H <sub>2</sub>	N <sub>2</sub>	CO	NO	CH <sub>4</sub>	CO <sub>2</sub>	N <sub>2</sub> O	SiF <sub>4</sub>
H <sub>2</sub> P	18	25	-	-	2.6	0.6	-	-	tr	-
	21	40	-	-	5.7	1.8	-	-	0.9	1.0
	21	55	-	-	10.1	24.6	-	-	-1	1.9
	18	70	-	-	-	-	tr	24.7	24.9	-
										N <sub>2</sub> F <sub>4</sub> (tr), HF (4.0), NF <sub>3</sub> (tr)
HAP	46	25	-	tr	tr	-	-	-	-	-
		40	-	1.3	0.7	-	-	0.7	-	-
		60	-	-	-	Sample Leaked	-	-	-	-
		80	11.5	7.8	43.0	-	tr	2.5	8.9	-
										CH <sub>2</sub> O <sub>2</sub> CH <sub>3</sub>
46	25	-	0.5	tr	tr	-	tr	-	-	1.5
		40	-	0.3	0.2	-	-	tr	-	-
		60	220.0	6.6	19.3	-	-	8.8	29.6	-
		80	172.0	13.4	29.5	-	tr	12.4	24.8	-
										CH <sub>2</sub> O <sub>2</sub> CH <sub>3</sub>
101	25	-	-	tr	-	-	-	-	-	2.5
		40	tr	4.8	3.6	-	-	1.4	2.1	-
		60	13.2	5.9	23.8	-	tr	8.7	36.6	-
		80	36.3	54.5	6.4	-	tr	16.0	12.3	-
										CH <sub>2</sub> O <sub>2</sub> CH <sub>3</sub>
HP-2	25	-	-	-	-	-	-	-	-	1.5
		40	-	1.8	0.6	-	-	0.3	0.5	-
		60	9.9	6.8	23.8	-	tr	10.9	31.7	-
		80	24.8	6.8	53.8	-	tr	18.0	30.9	-
										CH <sub>2</sub> O <sub>2</sub> CH <sub>3</sub>
34	25	-	20.1	3.2	-	-	1.0	tr	-	0.8
		40	-	3.3	1.3	-	-	1.0	1.6	-
		55	tr	4.4	17.4	-	-	24.2	14.3	-
		70	tr	39.8	46.6	-	-	35.7	11.4	-
										HF (5.0), HF (6.5)

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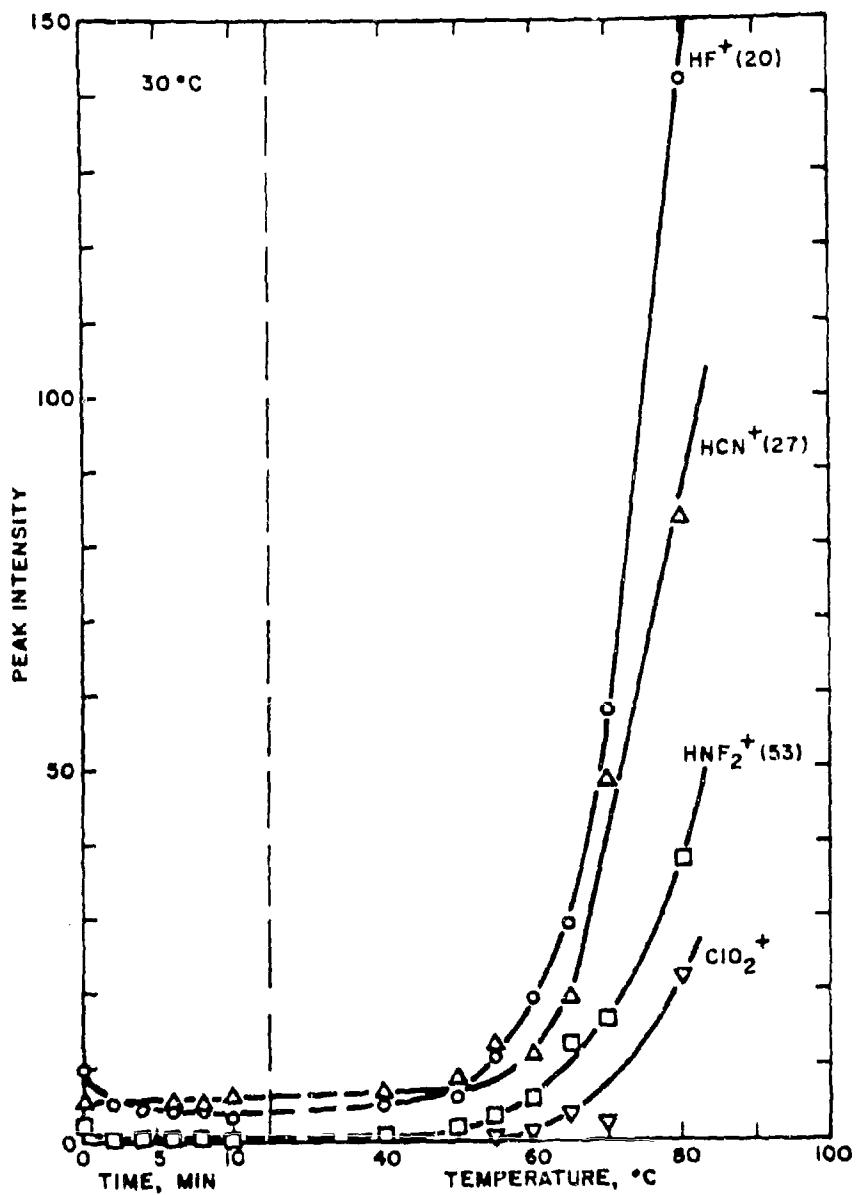


Figure VI-12 - Variation in Peak Intensity as a Function of Temperature  
for Species Observed from P-BEP/HAP Mixtures

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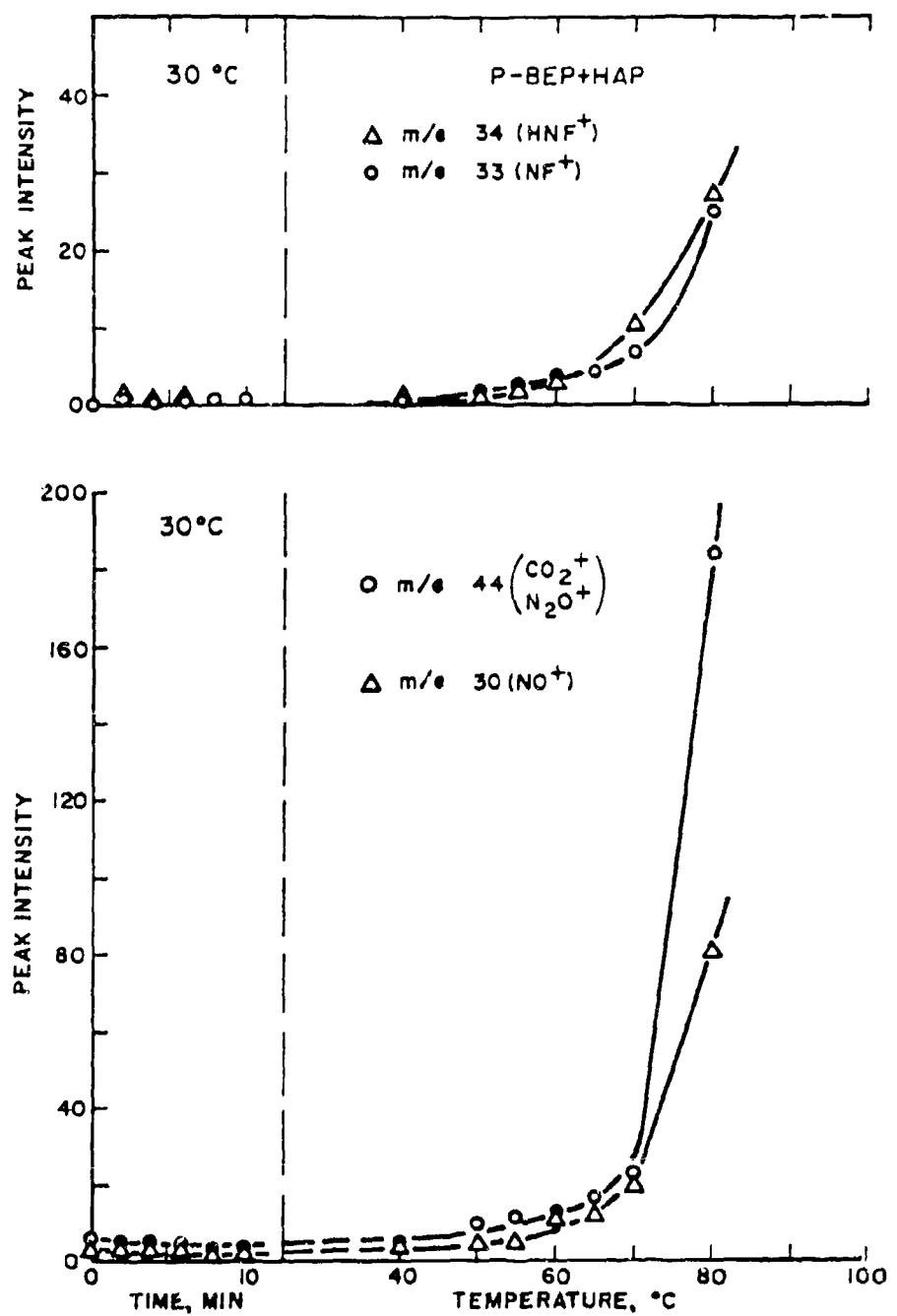


Figure VI-13 - Variation in Peak Intensity as a Function of Temperature

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from the thermal degradation were found to be HF, HCN, CO<sub>2</sub>, N<sub>2</sub>O, and HNF<sub>2</sub>. Perchloric acid was also present in the gaseous phase as evidenced by the m/e values characteristic of the acid.

TABLE VI-VIII

PRINCIPAL m/e VALUES OBSERVED AT 80°C

<u>m/e</u>	<u>Ions</u>	<u>m/e</u>	<u>Ions</u>
20	HF <sup>+</sup>	34	NH <sub>4</sub> O <sup>+</sup> , HNF <sup>+</sup>
26	CN <sup>+</sup>	36	HCl <sup>+</sup>
27	HCN <sup>+</sup>	43	C <sub>2</sub> H <sub>3</sub> O <sup>+</sup>
28	N <sub>2</sub> <sup>+</sup> , CO <sup>+</sup>	44	CO <sub>2</sub> <sup>+</sup> , N <sub>2</sub> O <sup>+</sup>
29	CHO <sup>+</sup> , C <sub>2</sub> H <sub>5</sub> <sup>+</sup>	45	C <sub>2</sub> H <sub>5</sub> O <sup>+</sup>
30	NO <sup>+</sup>	52	NF <sup>+</sup>
31	CF <sup>+</sup> , NH <sub>2</sub> O <sup>+</sup>	53	HNF <sub>2</sub> <sup>+</sup>
32	O <sub>2</sub> <sup>+</sup> , NH <sub>2</sub> O <sup>+</sup>	67	ClO <sub>2</sub> <sup>+</sup>
33	NH <sub>3</sub> O <sup>+</sup> , NF <sup>+</sup>		

(C) Very small quantities of HF were initially present in the P-BEP as shown by the curve for the evolution of HF. The curve rapidly levels and remains at a constant value with time. As the temperature is increased, no appreciable change occurs up to 50°C. In the temperature region of 50°C to 65°C, the evolution increases rather rapidly and above this temperature extensive quantities of HF are being produced.

(C) The curves for the evolution of HCN and HNF<sub>2</sub> are quite similar to the one observed for HF. The evolution of both species appears to remain relatively constant and at a low level until the sample temperature reaches 50°C. Above this temperature, the evolution becomes quite pronounced but to a much lesser extent than in the case of HF. The ions at m/e values of 33 and 34 follow the curve for the evolution of HNF<sub>2</sub> up to 70°C. Above that temperature, m/e 33 (NF<sup>+</sup>) appears to be increasing at a greater rate than that for HNF<sup>+</sup> (m/e = 34). This behavior would be anticipated since NF<sub>3</sub> is evolved from P-BEP/HAP mixtures at 70°C (Table VI-III). Thus, a contribution of m/z 33 but not to m/e 34 would be expected.

(C) Long term studies (18 to 21 days) of P-BEP/HAP mixtures have shown that CO<sub>2</sub> and N<sub>2</sub>O are produced in essentially equal quantities over the temperature range of 25 to 70°C. Furthermore, the total quantity of the two gases produced at 40, 55 and 70°C was 2, 4 and 50 ml. of gas/g P-BEP, respectively. These results are in very good agreement with the curves obtained for m/e 44 and 30.

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(C) In summary, little gas evolution occurred in this system at ambient temperatures (~ 30°C) for times up to 10 min. In the temperature range of 50 to 70°C, the quantity of HF, HCN, N<sub>2</sub>O and HNF<sub>2</sub> gas evolution increased appreciably, and above 70°C the rate of evolution became quite rapid. Chlorine dioxide did not appear until 55°C and increased in intensity until the study was stopped at 80°C.

(C) P-BEP/HP-2: The principal m/e values produced by the thermal degradation of a mixture of P-BEP and HP-2 at 120°C are shown in Table VI-IX. This study was conducted over the temperature range of ambient to 120°C. Obviously, the assignment of other ions can be made to some m/e values; however, the designated ions represent those which are thought to be the major contributor to the particular mass value.

TABLE VI-IX

PRINCIPAL m/e VALUES OBSERVED AT 120°C

<u>m/e</u>	<u>Ions</u>	<u>m/e</u>	<u>Ions</u>
20	HF <sup>+</sup>	33	HF <sup>+</sup>
26	CN <sup>+</sup>	34	HNF <sup>+</sup>
27	HCN <sup>+</sup>	36	HCl <sup>+</sup>
28	N <sub>2</sub> <sup>+</sup> , CO <sup>+</sup>	43	C <sub>2</sub> H <sub>3</sub> O <sup>+</sup>
29	N <sub>2</sub> H <sup>+</sup>	44	CO <sub>2</sub> <sup>+</sup> , N <sub>2</sub> O <sup>+</sup>
30	N <sub>2</sub> H <sub>2</sub> <sup>+</sup> , NO <sup>+</sup>	52	NF <sub>2</sub> <sup>+</sup>
31	N <sub>2</sub> H <sub>3</sub> <sup>+</sup>	53	HNF <sub>2</sub> <sup>+</sup>
32	O <sub>2</sub> <sup>+</sup> , N <sub>2</sub> H <sub>4</sub> <sup>+</sup>	67	ClO <sub>2</sub> <sup>+</sup>

(C) The variation in peak intensity as a function of time (at 30°C) and temperature for a number of the species evolved during the thermal degradation of the mixture is shown in Figures VI-14 to VI-16. The principal gaseous products observed from the thermal degradation of the mixture were HF, HCN, HNF<sub>2</sub>, N<sub>2</sub>O and CO<sub>2</sub>. Perchloric acid was also found in the gaseous phase as noted by the formation of ions characteristic of the acid.

(C) The most striking feature of this study was the evolution of gaseous products at ambient temperatures. In almost all cases, the evolution reached a maximum within 7 to 10 min. from the time the sample was inserted and then the gas elimination decreased with time to a relatively constant value after 30 min.

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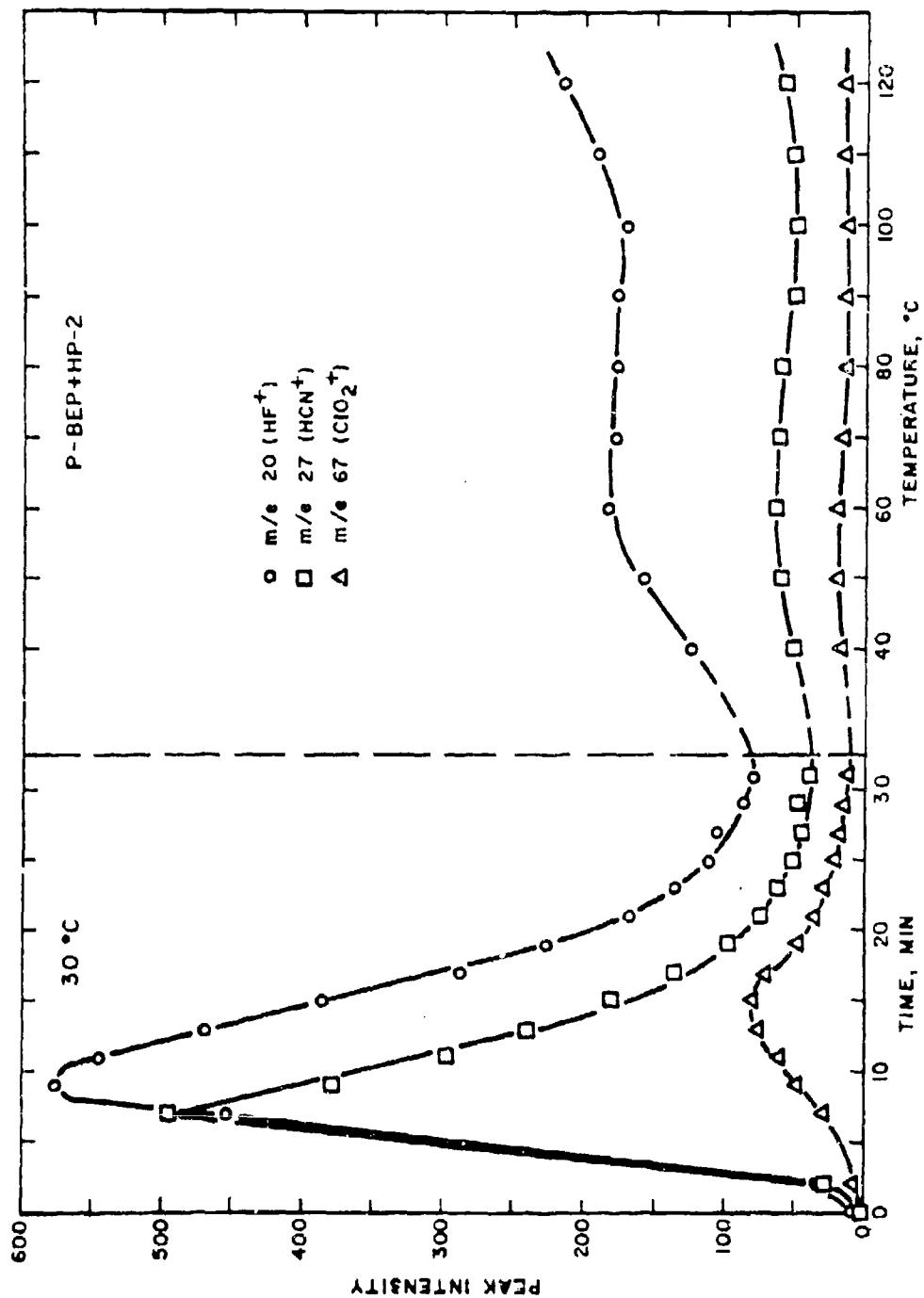


Figure VI-14 - Variation of Peak Intensity With Temperature for Species from P-BEP/HP-2 Mixtures

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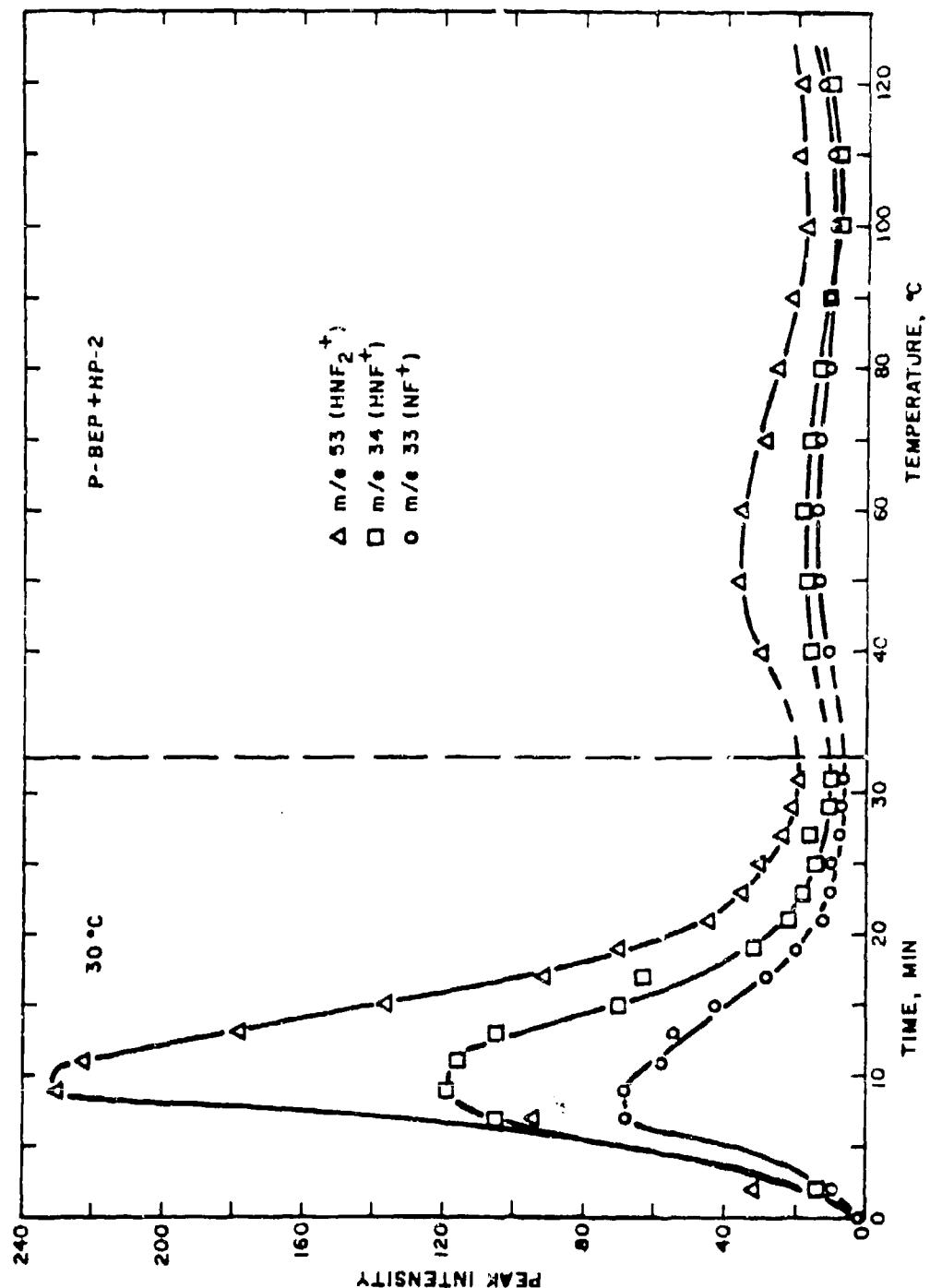


Figure VI-15 - Variation in Peak Intensity as a Function of Temperature

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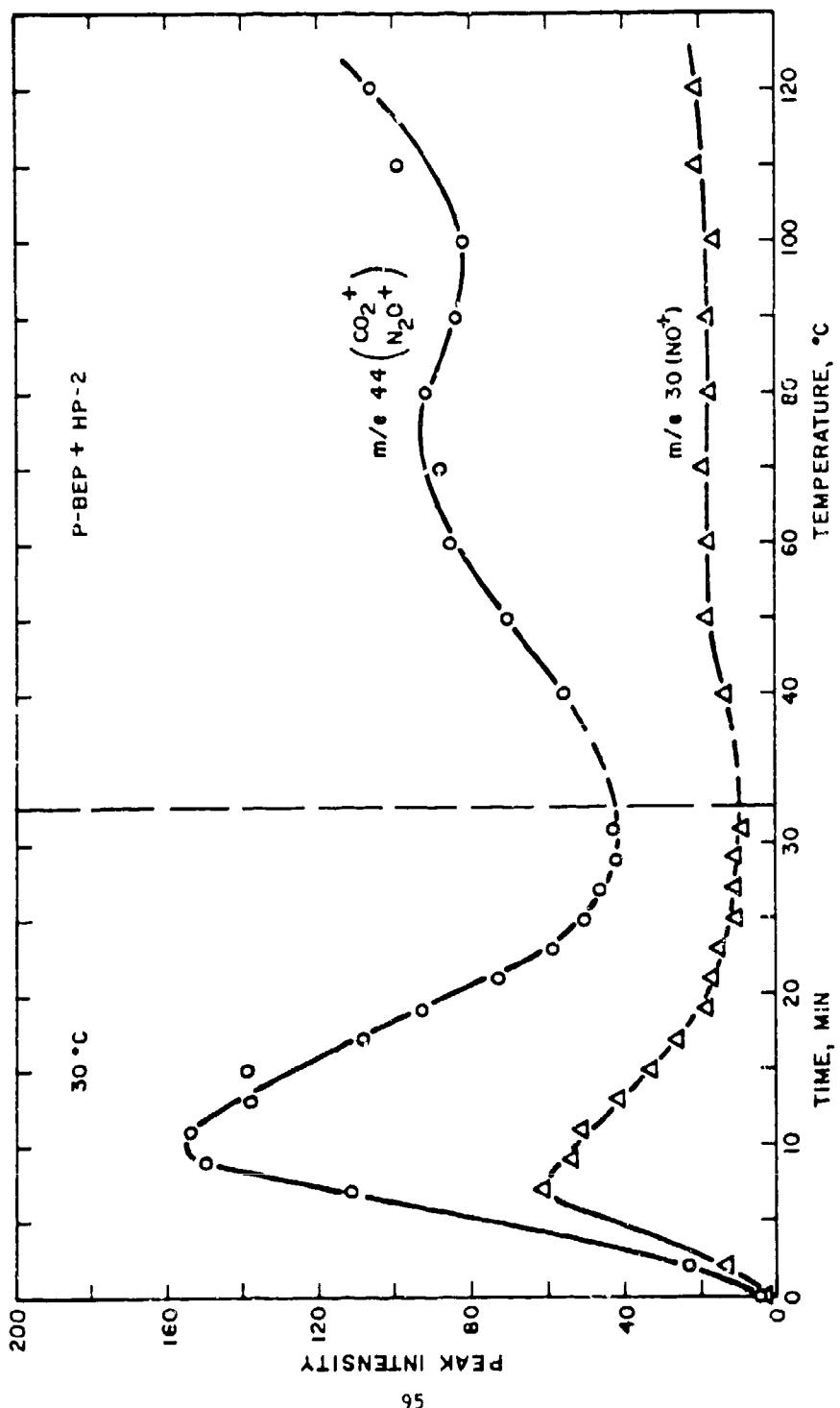


Figure VI-16 - Variation of Peak Intensity With Temperature for  $m/e$  44 and 30

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(C) With increasing temperature, the evolution of HF became more pronounced up to 60°C and then remained at a relatively constant value up to 100°C. Above 100°C, the evolution again increased with increasing temperature. For HCN and HNF<sub>2</sub>, the quantity of gas increased slowly with temperature to a broad, shallow maximum in the range of 55 to 65°C and then decreased slowly with temperature up to 100°C. Above this temperature, the evolution of both species increased slowly with increasing temperature. The curves for m/e 33 and m/e 34 follow the curve for the evolution of HNF<sub>2</sub> up to ~ 100°C. At temperatures above 100°C, the curve for m/e 33 appears to be increasing more rapidly than that for HNF<sup>+</sup>. This indicates that perhaps other NF species are being produced at temperatures above 100°C.

(C) As previously noted, long-term (31 days) studies of P-BEP/HP-2 mixtures at 40, 55 and 70°C have shown that CO<sub>2</sub> evolution increases with temperature, while N<sub>2</sub>O evolution remains essentially constant from 55 to 70°C. If the species at m/e 30 (NO<sup>+</sup>) can be assumed to be indicative of N<sub>2</sub>O evolution, these results are in good agreement with the long term studies. The curve for m/e 30 does increase with temperature up to 50°C and then remains at a relatively constant value for the duration of the study. For m/e 44, evolution increases with temperature to a maximum at 70 to 80°C and then decreases with increasing temperature up to 100°C. An increase in the evolution of the species contributing to m/e 44 was noted at temperatures above 100°C.

(C) 4. P-BEP/curing agent compatibility: Preliminary studies with P-BEP/curing agent systems were undertaken using infrared techniques. Curing agents considered were an isocyanate (DDI) and an epoxide (ERLA-4221). Results are presented in Table VI-X. The temperatures used for these studies are higher than those likely to be encountered during cure of a propellant.

(C) The P-BEP/curing agent ratio was approximately 1:1 by weight. The materials were studied before the system cured. After heating for one day (or overnight) the product was a fairly hard solid in both cases.

(C) The P-BEP/DDI and P-BEP/ERLA-4221 systems gave about 10% of the quantities of products evolved from analogous pure P-BEP systems. These preliminary results seem to indicate that P-BEP is less susceptible to thermal degradation in a cured system than it is by itself.

(C) Compatibility studies between P-BEP and the curing agents DDI and ERLA-4221 were continued for longer terms. Mixtures containing four parts P-BEP to one part DDI and eight parts P-BEP to one part ERLA-4221 were prepared, placed in metal tubes, and held at constant temperatures for two to seven weeks. The results are presented in Table VI-XI.

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TABLE VI-X

VOLATILE DECOMPOSITION PRODUCTS AS DETERMINED BY INFRARED  
FOR P-BEP/CURING AGENT SYSTEMS

Curing Agent	Time (days)	T (°C)	CH <sub>2</sub> Cl <sub>2</sub> (ml/g)	HF (ml/g)	HNF <sub>2</sub> (ml/g)	HCN (ml/g)	N <sub>2</sub> O (ml/g)	CO <sub>2</sub> (ml/g)
DDI	0.7	80	1.9	1	-	0.9	-	-
	0.7	80	2.0	-	-	1.2	-	-
	0.7	80	1.7	-	-	0.5	-	-
	0.7	80	0.7	-	-	-	-	-
	1	85	1.5	-	-	-	-	-
ERLA- 4221	0.7	80	0.5	-	tr*	0.2	-	-
	0.7	80	2.9	1	0.05	2.1	-	-
	1	85	2.4	-	-	-	-	-

\* Trace quantities.

(C) These studies were conducted with considerable excess curing agents to accentuate any reaction between P-BEP and a curing agent in an actual propellant which might contain excess curing agent.

(C) These studies indicate that the curing agents do not increase the evolution of gaseous products above that observed for P-BEP alone over comparable time periods. An important observation from these results is the absence of HCN and HF, as contrasted with the presence of these gases in the previous studies of P-BEP alone.

(U) The effect of HF on isocyanates has been studied to show its effect on the isocyanate functionality. In all cases, reaction of isocyanates and HF was readily observed. Isocyanates studied include DDI, HMDI, TDI, and phenyl isocyanate. When HF is bubbled into these liquids, they turn into solids, with the exception of DDI which turns into a very viscous liquid. It was also observed that HF and TDI react at room temperature to give COF<sub>2</sub>.

(U) Mechanistically, we believe that HF acts toward the isocyanate as does H<sub>2</sub>O and may account for some of the problems encountered in attempts to cure P-BEP with an isocyanate. We suggest that the following reactions occur:

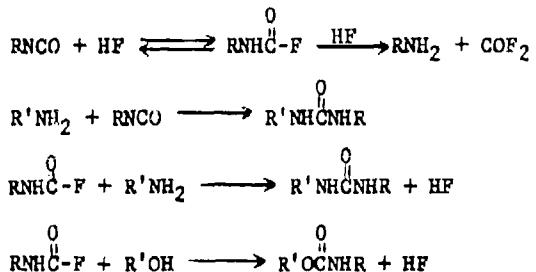
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TABLE VI-XI

GASEOUS PRODUCTS FROM P-BEP/CURING AGENT MIXTURES

Time (days)	Temp. (°C)	N <sub>2</sub>	CO	CO <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	N <sub>2</sub> O	Others
P-BEP-DDI							
27	25	0.1	(t)	0.2	2.2	-*	
	40	0.3	(t)	0.8	-	-	
	55	-	-	-	2.2	-	
	70	14.0	2.7	3.9	2.2	0.1	H <sub>2</sub> , CH <sub>4</sub>
50	25	14.6	-	3.0	2.6	-	
	40	0.7	0.3	2.1	2.2	tr	
	55	0.7	0.4	2.4	2.4	0.2	H <sub>2</sub> , CH <sub>4</sub>
	70	1.8	2.4	6.4	3.0	0.6	H <sub>2</sub> , CH <sub>4</sub>
P-BEP/ERIA-4421							
14	25	-	(t)	0.2	2.1	-	
	40	0.2	0.06	0.2	1.9	tr	
	55	5.2	1.3	1.1	1.9	0.4	H <sub>2</sub>
	70	4.3	2.5	3.8	2.2	0.7	H <sub>2</sub>
92	25	0.3	0.1	0.2	2.2	tr	-
	40	1.0	0.2	0.7	2.1	0.3	-
	55	1.7	1.6	1.3	2.0	0.4	H <sub>2</sub> , CH <sub>4</sub>
	70	18.7	8.5	3.8	2.1	0.4	H <sub>2</sub> , CH <sub>4</sub>

\* (-) Denotes that no detectable quantities of the compound were found in the gaseous mixture.



(C) In summary, the curing agents did not significantly increase the evolution of gaseous products above that observed for P-BEP alone. In contrast

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to the results from pure P-BEP, no fluorinated gaseous products (HF) were observed from these mixtures. It was shown that HF evolved from the P-BEP would very probably undergo reaction with the curing agent. The evolution of gaseous products from these mixtures was slow compared to normal curing times and probably will not present any significant problem in this respect. Additional studies are needed to define curing reactions and to determine whether problems associated with the attack on the curing agent or catalyst by P-BEP decomposition products can be overcome.

E. Summary of Results

(U) 1. P-BEP stability: Chemical changes in neat P-BEP together with the identification and measurements of the rates of formation of gaseous decomposition products were studied to obtain a more definitive picture of the mode of P-BEP decomposition. The results of this investigation complement and supplement the findings of other investigators who have looked at P-BEP stability. The following conclusions regarding P-BEP stability can be drawn from this study.

(C) a. It is extremely difficult to remove the last traces of methylene chloride from neat P-BEP. Vacuum stripping at  $10^{-4}$  torr and 50°C for 2 hr. will leave approximately 1 wt. % residual methylene chloride in the polymer.

(C) b. P-BEP shipped in a methylene chloride solution contains small quantities of acetone and hydrocarbon impurities. These impurities can be removed by precipitating the P-BEP from methylene chloride with Freon-11. Trace quantities of Freon-11 are left in P-BEP purified by this procedure.

(C) c. The principal low temperature gaseous decomposition products obtained from P-BEP are HF, HCN and  $\text{HNF}_2$ . The relative quantities of these gases as detected by IR and direct inlet mass spectrometry, were HF > HCN >  $\text{HNF}_2$ .

(C) d. The rate of HF evolution increases slowly as the temperature is raised from 30 to 70°C. A plot of the log ( $\text{HF}^+$ ) versus 1/T gives a straight line over this temperature range. This line crosses the temperature intercept at 5°C, indicating that HF elimination below this temperature is negligible. The rate of HF elimination increases rapidly above 85°C which suggests a change in mechanism of HF elimination.

(C) e. The rate of HCN elimination increases slowly up to 85°C. Above 85°C the rate increases significantly. A plot of log (m/e 27 intensity) versus 1/T indicates that HCN can be liberated at or below room temperature once dehydrofluorination to form the nitrile functionality has occurred.

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(C) f. Difluoramine appears as a decomposition product at ~ 50°C, increases slightly up to 80-85°C, then increases more rapidly with temperature.

(U) g. In the vicinity of 80-85°C P-BEP decomposition becomes very complex, and significant quantities of a variety of gaseous decomposition products are liberated.

(C) h. CO, CO<sub>2</sub>, NO, N<sub>2</sub>O, and N<sub>2</sub> are secondary products observed from P-BEP. These gases begin to appear in trace quantities at 40°C after 4 days.

(U) i. Little chemical change was detected by IR in P-BEP polymer in 16 hr. below 130°C.

(C) 2. P-BEP/oxidizer compatibility: The compatibility of P-BEP with AP, HAP and HP-2 was investigated.

(U) a. Ammonium perchlorate is two orders of magnitude more compatible with P-BEP than either HAP or HP-2. It does not appear to promote the decomposition of P-BEP below 80°C and may in fact have a stabilizing effect. HF, HCN and HNF<sub>2</sub> are not liberated as quickly at 80°C in the P-BEP/AP mixture as from neat P-BEP.

(U) b. P-BEP decomposition is accelerated appreciably by HAP and HP-2. Both oxidizers appear to promote C-N bond cleavage resulting in formation of N<sub>2</sub>F<sub>4</sub>, which is not observed as a P-BEP decomposition product in the absence of oxidizers.

(U) c. Methylene chloride reacts out of the system in the presence of both HAP and HP-2.

(U) d. The end reaction products CO, CO<sub>2</sub>, N<sub>2</sub>, and N<sub>2</sub>O are formed in much larger quantities in the presence of HAP or HP-2 than in the presence of AP.

(C) 3. P-BEP/curing agent compatibility: Both DDI and ERLA-4221 appear to be reasonably compatible with P-BEP. Less gaseous reaction product is observed in the presence of the curing agents than when neat P-BEP is heated. We anticipate that DDI may react with HF and HNF<sub>2</sub> and studies of the effect of the P-BEP decomposition products on the curing agents are needed.

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(This page is unclassified.)

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## VII.

### ENERGETIC PLASTICIZERS

(C) The stability and compatibility of the plasticizers TVOPA and P-722 were investigated. Their stability and their compatibility with the oxidizers HAP and AP, and with the ethyl acrylate-acrylic acid copolymer are discussed in this section of the report. The compatibility of these energetic plasticizers with AlH<sub>3</sub> is discussed in Section VIII.

#### A. Experimental Techniques

(C) TVOPA used in these studies was supplied by the Rohm and Haas Company as a 9% solution in Freon and chloroform. The solvent was removed under vacuum. No additional purification was carried out.

(C) P-722 was supplied by the Shell Development Company. The material had a reported purity of > 99.5% and was shipped as a 20% solution in methylene chloride. The solvent was removed under vacuum and the material used without further purification.

(U) The analytical techniques used for these studies were described in Section IV. These studies were conducted in passivated steel test cells.

#### B. Experimental Results

(C) 1. Plasticizer stability: Neat P-722 did not yield appreciable quantities of gaseous decomposition products at ambient or 40°C for time intervals up to 340 days (Table VII-I). At 55°C, only small quantities of gases were formed over the same time period. Samples stored at 70°C for approximately 1 year (340 days) yielded a total gas volume of about 36 ml/g of P-722; the gases were primarily CO, CO<sub>2</sub>, and N<sub>2</sub>O with small amounts of H<sub>2</sub> and N<sub>2</sub>.

(C) Little gas evolution was observed from TVOPA after 310 days at 70°C. Figure VII-1 shows gas evolution as a function of temperature for both plasticizers.

(C) 2. Plasticizer/oxidizer compatibility: Mixtures of P-722 and AP showed very small quantities of gaseous products of all four temperatures after 326 days. The same result was observed for P-722/HAP mixtures at 25 and 40°C over the same time interval. At 55°C, the P-722/HAP mixtures evolved a total volume of gaseous products equal to 37 ml/g of P-722, with

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TABLE VII-I

P-722/OXIDIZER COMPATIBILITY STUDIES

Material	Time (days)	Temp. (°C)	Evolved Gases (ml/g plasticizer)						
			H <sub>2</sub>	N <sub>2</sub>	CO	NO	CH <sub>4</sub>	CO <sub>2</sub>	N <sub>2</sub> O
None	39	25	-	-	-	-	-	-	-
		40	-	-	tr	-	-	-	-
		55	-	tr	tr	-	-	tr	-
		70	-	0.2	0.04	-	-	0.2	-
	140	25	-	0.07	tr	-	-	tr	-
		40	-	0.08	tr	-	-	0.2	-
		55	-	0.3	0.03	-	-	0.2	tr
		70	tr	0.8	1.0	tr	tr	9.5	4.3
	340	25	-	-	-	-	-	-	CH <sub>2</sub> Cl <sub>2</sub>
		40	-	-	tr	-	-	tr	-
		55	tr	0.5	0.4	-	-	0.8	1.4
		70	4.0	2.2	8.8	-	tr	11.2	9.6
AP	35	25	-	-	-	-	-	-	-
		40	-	0.2	0.3	-	-	1.3	-
		55	-	0.1	tr	-	-	tr	-
		70	-	0.5	0.2	-	-	1.4	tr
	95	25	-	0.2	0.08	-	-	0.4	-
		40	-	0.3	0.1	-	-	0.6	tr
		55	-	1.6	tr	-	-	1.4	0.6
		70	-	4.3	1.2	-	-	4.3	1.8
	326	25	-	-	-	-	-	-	-
		40	-	-	-	-	-	-	SiF <sub>4</sub> (9.5)
		55	tr	2.9	0.2	0.2	-	0.2	1.5
HAP	35	25	-	-	-	-	-	-	-
		40	-	0.3	tr	-	-	tr	tr
		55	-	1.4	1.3	-	-	9.3	29.4
		70	tr	2.8	7.8	-	-	25.1	32.3
	98	25	-	0.2	tr	-	-	tr	-
		40	-	1.0	0.2	-	-	1.9	0.9
		55	-	2.8	0.6	-	-	5.0	7.0
		70	tr	16.1	21.1	tr	-	63.3	126.0
	326	25	-	-	-	-	-	-	SiF <sub>4</sub> (6.7)
		55	tr	7.9	2.9	-	-	6.8	19.6
		70	tr	48.6	13.2	0.4	-	19.4	85.1

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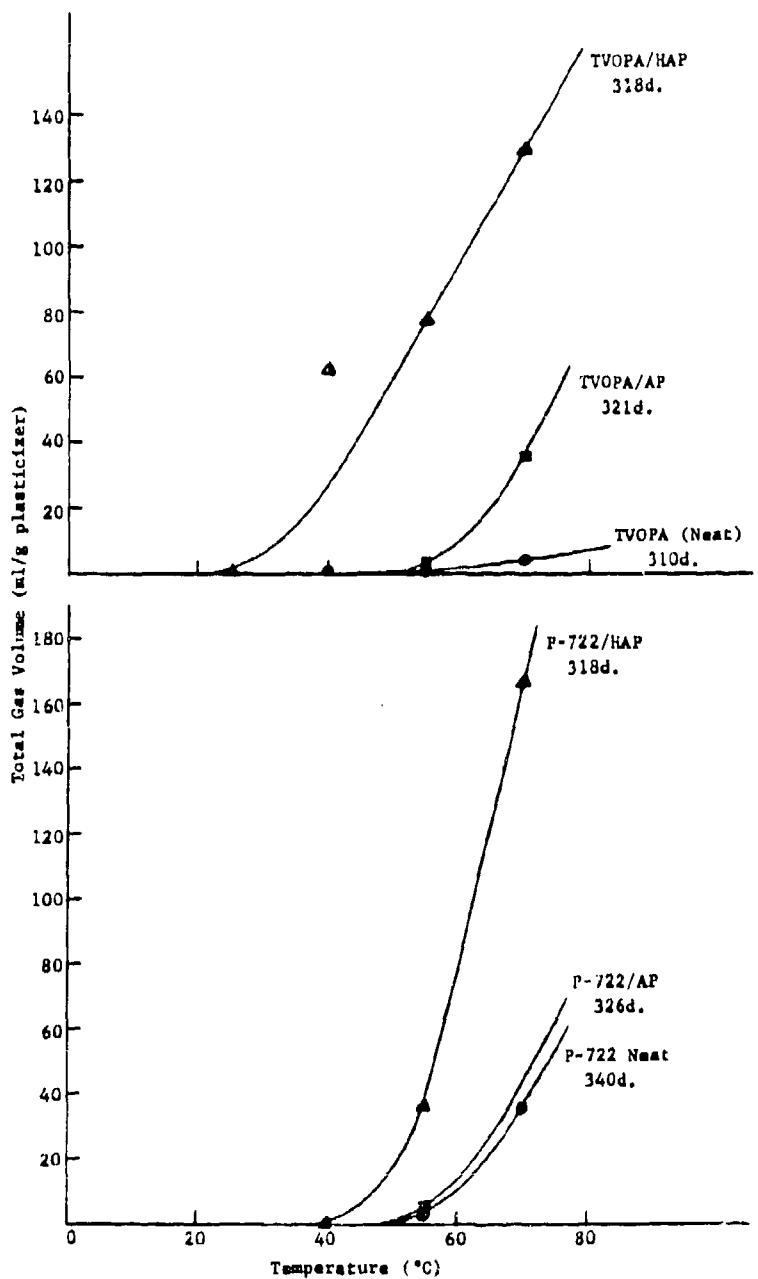


Figure VII-1 - Total Gas Evolved from Plasticizer/Oxidizer Mixtures

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approximately 50% of this quantity attributable to N<sub>2</sub>O. A large volume of decomposition products was observed for the same system at 70°C with N<sub>2</sub>, CO, CO<sub>2</sub>, and N<sub>2</sub>O as the principal components. After 326 days, very little degradation of AP/P-722 mixtures was observed at 55°C.

(C) In terms of the comparative compatibility of AP and HAP with P-722, both oxidizers are compatible at 25 and 40°C for time periods of 326 days. At the two higher temperatures, the P-722/AP mixtures are considerably more stable than the corresponding mixtures with HAP over the same time intervals.

(C) Mixtures of TVOPA with AP yielded somewhat larger quantities of gaseous decomposition products at 70°C over a time interval of 321 days than did neat TVOPA (Table VII-II). No decomposition products were observed at either 25 or 40°C and only minor quantities of N<sub>2</sub>, CO and CO<sub>2</sub> were found at 55°C. For the TVOPA/HAP system, the quantity of gaseous decomposition products evolved from the mixture at 70°C was considerably larger than the quantity observed from either TVOPA alone or the TVOPA/AP mixture. These results are analogous to the data from the P-722 systems, in which HAP produced considerably larger quantities of gas at 70°C than either the neat P-722 or the P-722/AP mixture over corresponding time intervals. The TVOPA/HAP mixture showed a consistent decrease in total gas volume with decreasing temperature; at ambient temperatures, no gaseous decomposition products were found after a 318-day time period.

(C) In general, TVOPA and P-722 exhibit comparable stabilities after 300 days at 25, 40, and 55°C. At 70°C TVOPA appears to be slightly more stable than P-722. Both materials have adequate thermal stability for use in a propellant system. Compatibilities with the oxidizers, HAP and AP, are very similar. At 25, 40 and 55°C, P-722 appears to be slightly more compatible with the two oxidizers than TVOPA, while at 70°C TVOPA is better.

(C) 3. Plasticizer/binder compatibility: Data on the compatibility of the plasticizers with one of the acrylate binders, PU-105, was accumulated (Table VII-III). The results did not show a significant difference in compatibility of the two plasticizers. More gas was evolved from the plasticizer binder mixture, however, than from the plasticizer alone in similar time periods. The presence of hydrogen is probably due to evolution of HF and its reaction with the metal test vessel. Little or no evidence of HF evolution was observed in stability studies with the neat plasticizer.

C. Summary

(C) 1. Thermal stability: Both P-722 and TVOPA are relatively stable towards thermal degradation, particularly at temperatures up to 55°C for

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TABLE VII-II

TVOPA/OXIDIZER COMPATIBILITY STUDIES

<u>Material</u>	<u>Time (days)</u>	<u>Temp. (°C)</u>	<u>Evolved Gases (ml/g plasticizer)</u>					
			<u>H<sub>2</sub></u>	<u>N<sub>2</sub></u>	<u>CO</u>	<u>NO</u>	<u>CH<sub>4</sub></u>	<u>CO<sub>2</sub></u>
None	34	25	-	0.3	0.03	-	-	tr tr
		40	-	2.8	0.04	-	-	0.7 0.1
		55	tr	0.4	0.1	-	-	0.6 0.2
		70	tr	0.4	0.2	-	tr	1.1 0.2
	94	25	-	0.3	0.08	-	-	0.4 tr
		40	-	0.1	0.07	-	-	0.3 0.1
		55	-	4.3	0.3	-	-	0.4 0.2
		70	tr	0.7	0.4	-	-	1.0 0.3
	310	25	-	0.3	0.4	-	-	- -
		40	-	0.6	0.2	-	-	0.2 -
		55	-	0.5	0.4	-	-	0.1 0.3
		70	1.2	0.7	0.8	-	-	1.1 0.3
AP	30	25	-	-	-	-	-	-
		40	-	0.2	-	-	-	-
		55	-	0.3	tr	-	-	-
		70	-	1.1	1.0	-	-	1.2 tr
	90	25	-	0.2	tr	-	-	tr -
		40	-	0.5	0.1	-	-	0.2 tr
		55	-	1.7	1.4	-	-	2.1 0.3
		70	tr	1.0	2.2	-	tr	4.6 0.6
	321	25	-	-	-	-	-	-
		40	-	-	-	-	-	-
		55	-	1.5	0.7	-	-	0.4 -
		70	26.3	0.9	4.4	-	0.2	4.2 tr
HAP	25	25	-	-	-	-	-	-
		40	-	1.3	0.3	-	-	0.6 tr
		55	-	10.0	34.8	-	-	16.2 32.3
		70	tr	17.4	24.6	-	-	8.9 85.0
	86	25	-	1.4	0.1	-	-	1.4 tr
		40	-	9.8	3.8	-	-	3.9 0.6
		55	-	9.9	43.0	-	-	12.7 18.8
		70	tr	37.7	49.1	-	-	50.8 135.0
	318	25	-	-	-	-	-	-
		40	-	11.9	24.0	-	-	5.5 21.6
		55	tr	9.7	10.6	-	-	9.1 48.5
		70	6.6	17.6	23.4	-	tr	12.2 70.2

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TABLE VII-III

GASEOUS PRODUCTS FROM ACRYLATE BINDER/PLASTICIZER  
MIXTURES (PU-105)

Plasticizer	Time (days)	Temp. (°C)	Evolved Gases (ml/g of plasticizer)					
			H <sub>2</sub>	N <sub>2</sub>	CO	CO <sub>2</sub>	N <sub>2</sub> O	Other
TVOPA	33	25	-	-	-	-	-	-
		40	-	-	-	-	-	-
		60	-	0.4	0.2	0.2	-	-
		80	tr	2.0	0.6	0.4	-	-
	60	25	-	-	-	-	-	SiF <sub>4</sub> (7.4)
		40	tr	1.0	tr	-	-	SiF <sub>4</sub> (5.3)
		60	18.2	-	tr	-	-	SiF <sub>4</sub> (8.4)
		80	tr	7.5	13.2	5.6	1.1	ester, CH <sub>4</sub> (tr)
	123	25	-	-	-	-	-	-
		40	-	5.2	tr	tr	-	-
		60	-	-	-	0.3	-	-
		80	23.4	25.2	3.9	7.0	-	fluorocarbon, CH <sub>4</sub> (tr)
	180	25	-	-	-	-	-	-
		40	tr	-	tr	tr	-	-
		60	-	-	tr	tr	-	-
		80	3.7	0.7	1.1	3.7	-	CH <sub>3</sub> COC <sub>2</sub> H <sub>5</sub> , CH <sub>4</sub> (0.3)
P-722	33	25	-	-	-	-	-	SiF <sub>4</sub> (0.4)
		40	-	tr	tr	-	-	SiF <sub>4</sub> (0.4)
		60	-	-	-	-	-	-
		80	tr	0.3	tr	tr	tr	SiF <sub>4</sub> (5.7)
	61	25	-	-	-	-	-	SiF <sub>4</sub> (0.8)
		40	-	-	-	-	-	SiF <sub>4</sub> (1.4)
		60	-	-	-	-	-	SiF <sub>4</sub> (0.7)
		80	-	-	tr	0.1	tr	-
	180	25	tr	-	-	tr	-	-
		40	-	2.3	0.3	0.5	tr	-
		60	4.0	-	-	2.3	0.7	-
		80	4.0	1.6	0.5	2.9	1.6	NO (0.8)

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time intervals approaching 1 year. At 70°C for the same time period, P-722 evolves a total gas volume of approximately 36 ml/g, whereas the total gas volume for TVOPA is considerably less than this value.

(C) 2. Oxidizer compatibility: Neither AP nor HAP undergoes any significant reaction with P-722 at 25 or 40°C after a time interval of 326 days. At 55°C, the P-722/HAP mixture evolved approximately 37 ml. of gaseous products for the same time period. These products were N<sub>2</sub>, CO, CO<sub>2</sub>, and N<sub>2</sub>O. The mixture maintained at 70°C for 326 days evolved 167 ml. of gaseous products, consisting of N<sub>2</sub>, CO, CO<sub>2</sub>, and N<sub>2</sub>O. Only trace quantities of hydrogen were observed. Mixtures of P-722 and AP were found to evolve a smaller total volume of gases at the two higher temperatures than the corresponding mixtures with HAP.

(C) For a time interval of 318 days, the total volume of gaseous decomposition products evolved from the TVOPA/HAP system increased with temperature. At room temperature, no gaseous products were found; whereas at 70°C, a total volume of 130 ml/(g of TVOPA) was produced. After 321 days, AP/TVOPA mixtures showed little reaction at 25 and 40°C. At 55°C, minor quantities of gaseous products were observed and, for the sample maintained at 70°C, the total volume of gaseous products was 36 ml/(g of TVOPA). Aside from the total amount of gas evolved, there is a significant difference between the results from the HAP/TVOPA mixture and the AP/TVOPA mixture at 70°C. With HAP, the quantity of hydrogen evolved was relatively small with respect to the amounts of N<sub>2</sub>, CO, CO<sub>2</sub>, and N<sub>2</sub>O. In the AP/TVOPA mixture, hydrogen was the principal gaseous product at 70°C and accounted for over 70% of the total gas evolved. The hydrogen observed in these samples probably results from HClO<sub>4</sub> reaction with the metal cell.

(C) 3. Acrylate binder compatibility: Both plasticizers exhibit some reactivity with the acrylate binder at 60° and above. Little difference in relative reactivity could be detected after 180 days.

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VIII.

ALUMINUM HYDRIDE

(U) The stability of aluminum hydride ( $\text{AlH}_3$ ) and its compatibility with other propellant ingredients was investigated. The results of the studies can be briefly summarized as follows:

(C)  $\text{AlH}_3$  (Lot 11177B) which is magnesium doped, treated with DPA and hydrolyzed at pH 7 is the most stable sample of  $\text{AlH}_3$  studied. Thermally cycling  $\text{AlH}_3$  just prior to formulation into a propellant should improve the propellant's storage life.  $\text{AlH}_3$  shows good compatibility with HAP and AP after 70 days at 40°C. The plasticizers TVOPA and P-722 show good compatibility with  $\text{AlH}_3$  at 40°C. The P-BEP binder prepolymer is also reasonably compatible with  $\text{AlH}_3$  at 40°C; HF reacts rapidly with  $\text{AlH}_3$  to liberate hydrogen. Acrylate binder prepolymers pose no serious compatibility problems with  $\text{AlH}_3$  and may in fact improve its thermal stability.

A. Experimental

(C) Three lots of  $\text{AlH}_3$  were supplied by the Dow Chemical Company and used for the thermal stability studies: Lot 07035 was untreated, Lot 11236 was magnesium doped, and Lot 11177B was magnesium doped, DPA treated and hydrolyzed at pH 7. A second sample, Lot 08187A, treated in the same way as Lot 11177B was obtained. Lots 11177B and 08187A were used for all compatibility studies. The aluminum hydride was handled in the dry box and used without additional purification or treatment. The experimental procedures used for these studies are described in Section IV.

B. Experimental Results

(U) The stability of  $\text{AlH}_3$  and its compatibility with other propellant ingredients were studied by analyses for gaseous decomposition products.

1. Stability of LMH-1:

(C) a. Sealed tube studies: Samples of  $\text{AlH}_3$  as received were placed in evacuation glass break-seal tubes and immersed in constant temperature baths at 40, 60 and 80°C. Another set of samples were allowed to stand at ambient temperature. At time intervals of 15, 30, and 72 days, samples were withdrawn from the baths and analyzed for gaseous decomposition products. Using 50-mg. samples, the experimental technique employed is capable of detecting gas concentration indicative of 0.1% decomposition.

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Three different samples of AlH<sub>3</sub> were studied: Lot 07035 (untreated), Lot 11236 (Mg doped) and Lot 11177B (Mg doped, DPA treated and hydrolyzed at pH 7). There is a distinct difference in thermal stability between the three samples, with Lot 11177B being significantly better than either of the others.

(C) Hydrogen was observed from Lot 11177B only at 80°C after periods of 15 days. These results show no detectable decomposition after 30 days at 60°C and about 3% decomposition after 72 days at 60°C.

(C) Investigators at Dow (Ref. 1) observed approximately 1% decomposition of AlH<sub>3</sub> (Lot 11177B) in 30 days at 60°C. It is generally agreed that AlH<sub>3</sub> decomposes autocatalytically. The induction period associated with the decomposition was observed by Dow to vary significantly from sample-to-sample. A combination of the autocatalytic process, the poorly defined induction period and sample-to-sample variations all contribute to variations in these results between different laboratories. Based on these results all compatibility studies were conducted using Lot 11177B. The results of these studies are shown in Table VIII-I.

(C) b. Direct inlet mass spectrometry: The AlH<sub>3</sub> (Lot No. 11177B) utilized in this study was magnesium-doped and had been DPA and hydrolysis treated. Small samples of the material were placed in a gold crucible and inserted through an air lock to a distance of 5-7 mm. from the ion source. During evacuation of the samples, mass spectra were recorded at 70 ev. and m/e values observed for benzene, diethyl ether, 1,2-diphenylacetylene, 1,2-diphenylethylene, and 1,2-diphenylethane. In addition, the expected peaks corresponding to hydrogen, water, and air were observed. The time required for evacuation was normally 3-5 min.

(U) 1,2-Diphenylethane and 1,2-diphenylethylene result from the full and partial reduction of 1,2-diphenylacetylene. Analyses of the mass spectra showed an approximate composition of 55% diphenylacetylene, 15% diphenylethylene, and 30% diphenylethane. Thus, approximately one-half of the original DPA had been either partially or fully reduced.

(C) Preliminary studies had shown that when the sample was heated from ambient to 140°C, hydrogen constituted approximately 90% of the evolved gases. In view of these results, further studies were conducted in which the source ion current was recorded as a function of temperature. The rate of temperature increase during these studies was 2.5 to 3°C/min. Mass spectra were recorded periodically during the heating process and during abrupt changes in the source ion current. The results of a typical study are shown in Figure VIII-1. The maximum at 90-95°C was observed in several studies and was consistently within this same temperature range. Mass spectra obtained during this maximum showed an increase only in the hydrogen evolution.

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THERMAL STABILITY OF ALUMINUM HYDRIDE

<u>Sample</u>	<u>Temp.</u> (°C)	<u>Hydrogen Evolved ml/g AlH<sub>3</sub>*</u>		
		<u>7 Days</u>	<u>14 Days</u>	<u>31 Days</u>
Lot 07035 (untreated)	25	-	-	-
	40	-	-	0.4
	60	36.8	67.0	103.0
	80	515.0	800.0	340.0**
		<u>7 Days</u>	<u>14 Days</u>	<u>29 Days</u>
Lot 11236 (Mg. doped)	25	-	-	-
	40	-	-	-
	60	-	7.3	2.0
	80	22.4	80.0	83.0
		<u>15 Days</u>	<u>30 Days</u>	<u>72 Days</u>
Lot 11177B (Mg/DPA/hyd)	25***	-	-	-
	40***	-	-	-
	60***	-	-	33.2-39.8
	80***	11.5-20	67-79	123-173

\* 12.3 ml. of gas is equivalent to 1% decomposition.

\*\* Low quantity of H<sub>2</sub> measured probably due to a leak in the sample cell.

\*\*\* Duplicate samples.

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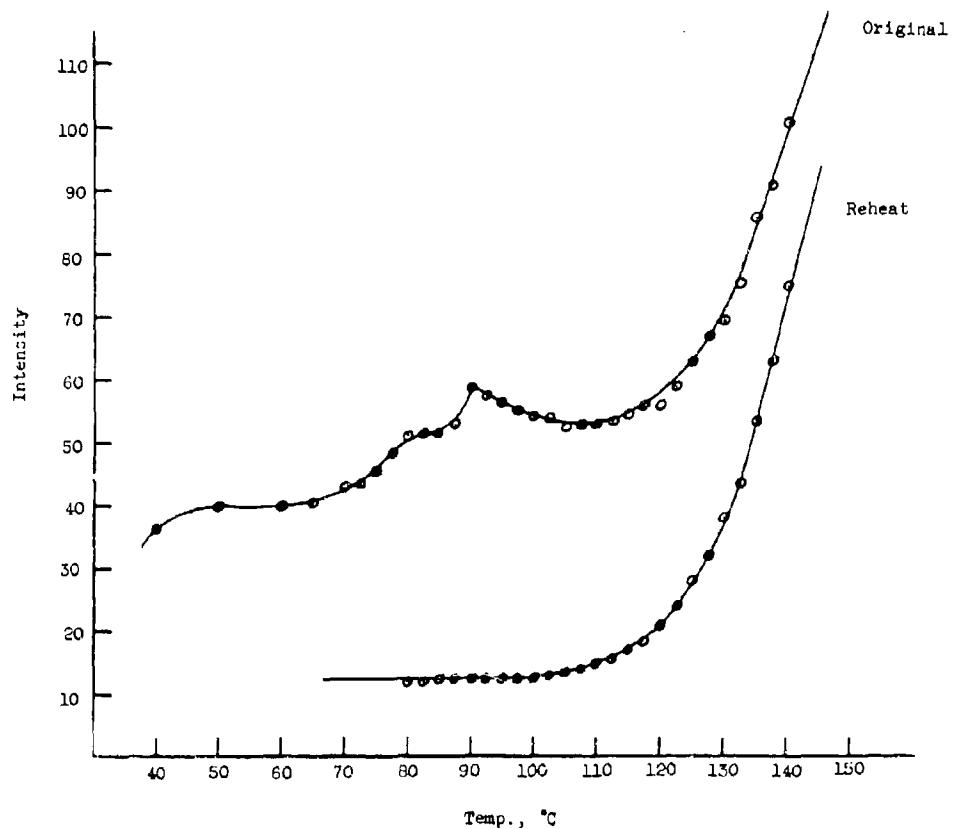


Figure VIII-1 - Mass Spectrometric Study of  $\text{AlH}_3$

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(C) After the temperature had reached 140°C, the crucible and contents were cooled to 80°C and the heating process repeated. The time required to cool the crucible and sample to 80°C was generally less than 1 min. These results show that the maximum observed originally has disappeared and that hydrogen evolution commences at approximately 110°C. At temperatures above 100°C, excellent agreement for the rate of hydrogen evolution is obtained between the original and reheated samples. The reduction in source ion current between the original and reheated sample is partially a result of sample decomposition. From the results one concludes that subjecting AlH<sub>3</sub> to a thermal cycling process may increase stability with respect to hydrogen evolution.

(C) A definite cause for the observed maximum cannot be stated unequivocally; potential sources are:

1. Absorbed hydrogen,
2. Adsorbed water reacting with the AlH<sub>3</sub>,
3. Presence of less stable crystalline forms of AlH<sub>3</sub>, and/or
4. Decomposition of other metal hydrides present as impurities (not LiH or MgH<sub>2</sub>).

It is unlikely that any one of the above alone is the complete answer. The reason for the maximum may be a combination of the above or a source other than those listed.

(U) 2. Compatibility: The compatibility of AlH<sub>3</sub> with HAP, AP, TVOPA, P-722, P-BEP, HF and the two acrylate binders, PU-103 and PU-105 was investigated. These materials were selected for study on the basis of discussions with propellant formulators and suggestions from the Rocket Propulsion Laboratory. With the exception of P-BEP, all components were used without further purification. All sample preparation was performed in a dry box.

(C) For those materials containing an N-F functionality (TVOPA, P-722, P-BEP) and for HF, approximately equal weights of the two ingredients were used. The mixture was placed in a passivated stainless steel tube, evacuated, and the valve closed. With HAP and the two acrylate binders, the ratio of AlH<sub>3</sub> to the second components was 1:1; the ratio of AlH<sub>3</sub> to AP was 1:2. These binary mixtures were placed in glass break-seal tubes, evacuated, and sealed. After remaining in constant temperature baths for the reported time intervals, the samples were withdrawn and analyzed for gaseous decomposition products by gas chromatography and infrared spectrometry.

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(U) The results of the analyses for the individual gaseous decomposition products are given in Table VIII-II. The reported values were obtained by integration of the data obtained by infrared spectroscopy and gas chromatography.

(C) a. Oxidizers: The compatibility of AlH<sub>3</sub> with hydrazylammonium perchlorate (HAP) and ammonium perchlorate (AP) has been investigated. Neither oxidizer appeared to promote the evolution of gaseous decomposition products at 25, 40, or 60°C for time periods up to 70 days. After 70 days at 80°C, the amount of hydrogen evolved from the AP/AlH<sub>3</sub> mixture is the same, within the limits of reproducibility, as that expected from pure AlH<sub>3</sub>. For the HAP mixture, at the same time interval and temperature, the hydrogen evolution is three to four times greater than would be expected from neat hydride. The data for the total volume of gaseous decomposition products are presented in Figure VIII-2.

(C) For time intervals up to 30 days, less hydrogen is evolved from AlH<sub>3</sub> oxidizer mixtures than from the neat hydride. It would appear unlikely that the oxidizer stabilizes the AlH<sub>3</sub> with respect to decomposition. The evolved hydrogen may react with the oxidizer to produce water, which would be absorbed in the solid mixture and not detected, or trace impurities (HClO<sub>4</sub>, metal ions) may catalyze the reduction of DPA.

(C) b. NF materials: The compatibility of AlH<sub>3</sub> with two NF plasticizers, P-722 and TVOPA, and the NF binder P-BEP was studied. Mixtures of each component with AlH<sub>3</sub> were studied in stainless steel test cells which had been previously passivated with ClF<sub>3</sub>. The volumes of the metal test cells are sufficiently small that the evolution of 50 ml. of gas/g of AlH<sub>3</sub> will increase the pressure within the cell to one atmosphere. Total gas evolved from mixtures of AlH<sub>3</sub> with two plasticizers and for the NF binder, P-BEP, for periods of 7 and 50 days are shown in Figure VIII-3. Actual gas compositions are given in Table VIII-II.

(C) In general, the data observed for both plasticizers are quite reproducible at 25, 40, and 60°C for all time intervals covered in this study. When averages of duplicate values are reported, the values for the major constituents generally agree within 5-7%. At 80°C, large quantities of hydrogen are evolved and the data do not appear to be reproducible. However, in many cases the pressure within the test cells has risen to 8 to 10 or more atmospheres. As a result of this high internal pressure, some cells developed leaks during storage. In other cases, the coloration of the mixture, after storage for the reported time interval, was indicative that the two samples did not react to the same extent. This factor can be exemplified by the two mixtures of P-722 and AlH<sub>3</sub>, which were maintained at 80°C for 8 days. The mixture that evolved 34.7 ml. of H<sub>2</sub> was gray in color; the mixture evolving 248 ml. of H<sub>2</sub> was a very black solid.

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TABLE VIII-II

**AlH<sub>3</sub> COMPATIBILITY STUDIES**

Material	Time (days)	Temp. (°C)	Evolved Gas in ml/g AlH <sub>3</sub>								
			H <sub>2</sub>	N <sub>2</sub>	CO	NO	CH <sub>4</sub>	CO <sub>2</sub>	N <sub>2</sub> O	SiF <sub>4</sub>	HCN
A2	7	25*	-**	-	-	-	-	-	-	-	-
		40*	-	-	-	-	-	-	-	-	-
		60*	-	-	-	-	-	-	-	-	-
		80	0.1	-	-	-	-	-	-	-	-
	15	25*	-	-	-	-	-	-	-	-	-
		40*	-	-	-	-	-	-	-	-	-
		60*	-	-	-	-	-	-	-	-	-
		80*	0.5	-	-	-	-	-	-	-	-
	28	25*	-	-	-	-	-	-	-	-	-
		40*	-	-	-	-	-	-	-	-	-
		60*	-	-	-	-	-	-	-	-	-
		80*	0.6	-	-	-	-	-	-	-	-
	70	25*	-	-	-	-	-	-	-	-	-
		40*	-	-	-	-	-	-	-	-	-
		60*	15.8	-	-	-	-	-	-	-	-
		80*	126	-	-	-	-	-	-	-	-
HAP	8	25*	-	-	-	-	-	-	-	-	-
		40*	-	-	-	-	-	-	-	-	-
		60*	-	-	-	-	-	-	-	-	-
		80*	0.1	-	-	-	-	-	-	-	-

\* Average of duplicate analyses.

\*\* (-) denotes that no gaseous material was observed.

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TABLE VIII-II (Continued)

Material (No. cl'd)	Time (days)	Temp. (°C.)	Evolved Gas in ml/g AlH <sub>3</sub>							
			H <sub>2</sub>	N <sub>2</sub>	CO	NO	CH <sub>4</sub>	CO <sub>2</sub>	N <sub>2</sub> O	SiF <sub>4</sub>
HAP	15	25*								
		40*								
		60*								
		80*	0.8	1.1	-	-	-	-	-	-
28		25*								
		40*								
		60*								
		80*	1.2	3.9	-	-	-	0.1	-	-
70		25*								
		40*								
		60*	tr	-	-	-	-	-	0.3	-
		80*	670	-	-	-	-	-	-	-
TVOPA	8	25*	-	-	-	-	-	-	-	-
		40	tr	0.6	0.2	0.1	-	-	0.3	-
		40	-	-	-	-	-	-	tr	-
		60*	-	-	-	-	-	-	-	-
		80	28.1	0.4	0.1	0.1	-	0.6	tr	-
		80	57.8	0.7	0.1	-	0.3	tr	tr	0.4
		15	25*	-	-	-	-	-	tr	-
		40*	-	tr	-	-	-	-	-	1.9
		60	tr	0.4	0.1	-	-	-	-	2.2
		60	tr	-	-	-	-	0.6	1.3	-
		80	111.5	1.3	0.1	-	-	-	-	5.3
		80	42.5	1.0	0.2	-	0.2	tr	-	-
							0.4	tr	-	3.4

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TABLE VIII-II (Continued)

Material (Concl'd)	Time (days)	Temp. (°C)	Evolved Gas in ml/g AlH <sub>3</sub>							
			H <sub>2</sub>	N <sub>2</sub>	CO	NO	CH <sub>4</sub>	CO <sub>2</sub>	N <sub>2</sub> O	SiF <sub>4</sub>
TVOPA	28	25*	-	-	tr	-	-	-	-	-
		40*	-	-	0.1	-	-	0.2	-	-
		60*	14.5	0.4	0.2	-	-	tr	-	2.2
		80	429	1.0	0.2	-	2.0	0.3	tr	-
		80	241	2.6	1.7	-	0.6	1.3	0.3	-
		56	25*	-	-	-	-	-	-	-
		40*	-	-	-	-	-	-	-	4.7
		60	23.4	6.7	0.1	-	-	-	tr	-
		60	53.5	0.8	0.1	-	0.4	-	-	2.4
		80	570	1.5	0.1	-	3.0	0.2	-	-
		80	229	1.1	0.2	-	4.0	0.2	-	8.7
P-722	8	25	5.0	-	-	-	-	tr	-	-
		25	-	-	-	-	-	No gaseous products	-	-
		40*	-	-	-	-	-	tr	-	-
		60*	tr	0.6	0.1	0.1	-	0.2	-	-
		80	34.7	0.1	0.1	tr	-	0.4	tr	0.8
		80	248	1.0	0.2	tr	tr	0.8	1.7	2.6
		15	25*	-	-	-	-	-	tr	-
		40*	-	tr	0.1	-	-	tr	-	-
		60*	tr	1.6	0.4	-	tr	0.7	tr	0.4
		80*	80.0	0.7	0.1	-	0.4	0.4	0.3	0.4

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TABLE VIII-II (Continued)

Material (Concl'd)	Time (days)	Temp. (°C)	Evolved Gas in ml/g AlH <sub>3</sub>							
			E <sub>2</sub>	N <sub>2</sub>	CO	NO	CH <sub>4</sub>	CO <sub>2</sub>	N <sub>2</sub> O	SiF <sub>4</sub>
<b>P-722</b>										
2.8	25*	-	-	-	-	-	-	-	-	-
40*	tr	0.4	tr	0.1	-	0.1	-	0.4	-	-
60*	3.0	0.4	tr	0.2	-	0.5	1.6	0.4	0.4	-
80	33C	1.1	0.2	-	-	-	-	-	-	-
80	676	10.4	1.7	0.7	6.1	3.5	2.2	-	-	-
56	25*	1.0	0.5	-	-	-	tr	-	tr	-
40*	tr	-	-	tr	-	-	tr	-	tr	-
60	25.1	0.8	0.1	tr	-	0.2	tr	tr	-	-
60	6.6	-	tr	-	-	-	-	9.0	-	-
80	385	3.4	0.5	0.3	2.4	1.3	1.3	12.8	-	-
80	41.8	4.1	1.0	0.2	0.4	3.2	1.4	-	0.8	HCO <sub>2</sub> CH <sub>3</sub>
<b>P-BEP</b>										
8	25*	-	tr	tr	-	-	-	tr	-	-
40*	tr	0.4	0.4	tr	tr	-	0.4	tr	0.2	-
60*	tr	1.4	0.2	-	-	0.2	tr	tr	1.0	-
80	206	7.3	1.3	-	0.2	0.4	0.2	1.7	2.2	-
80	585	2.3	0.8	-	0.6	0.8	tr	-	0.8	HF(tr)
15	25*	-	1.1	0.5	-	-	-	-	-	-
40*	tr	tr	tr	-	-	-	-	tr	-	-
60	tr	0.7	0.1	-	0.2	0.4	-	tr	2.5	HNF <sub>2</sub> (tr)
60	29.7	-	-	-	-	tr	-	-	-	-
80	297	0.5	0.2	-	0.2	0.4	-	1.7	0.8	-
80	760	1.5	0.8	-	2.5	1.0	tr	-	-	-

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TABLE VIII-II (Continued)

Material (Conc'l'd)	Time (days)	Temp. (°C.)	Evolved Gas in ml/g AlH <sub>3</sub>									
			H <sub>2</sub>	N <sub>2</sub>	CO	NO	CH <sub>4</sub>	CO <sub>2</sub>	N <sub>2</sub> O	SiF <sub>4</sub>	HCN	Others
P-BEP	28	25*	-	-	-	-	-	-	-	tr	-	-
	40*	-	0.1	tr	1.7	-	-	7.0	-	0.3	-	-
	60	79.2	1.9	-	-	tr	-	-	tr	5.7	HCO <sub>2</sub> CH <sub>3</sub>	-
	60	215	3.0	0.2	-	-	-	-	-	-	-	-
	80	1,195	0.8	0.2	-	2.0	0.3	-	-	-	-	-
	80	227	2.3	0.2	-	0.5	0.2	-	-	-	-	-
	5'	25*	-	-	-	-	-	-	-	6.3	-	-
	40	-	tr	-	-	-	-	-	-	-	-	-
	40	-	3.8	0.7	-	-	-	tr	-	1.4	1.2	-
	60	40.2	1.1	-	-	-	-	0.2	-	11.0	4.0	-
	60	5.0	1.1	tr	-	-	-	-	-	11.4	3.0	-
	60	755	0.6	0.1	-	3.0	-	-	-	-	-	-
	60	779	0.8	0.1	-	4.0	0.2	-	-	12.1	-	-
PU-103	30	25*	-	-	-	-	-	-	No gaseous products	-	-	-
	40*	-	-	-	-	-	-	-	No gaseous products	-	-	-
	60*	tr	-	-	-	-	-	-	-	-	-	-
	80	85	-	-	-	-	-	-	-	-	-	-
	80	114	-	-	-	-	-	-	-	-	-	-
	70	25*	tr	-	-	-	-	-	No gaseous products	-	-	-
	40	19	-	-	-	-	-	-	-	-	-	-
	60	-	-	-	-	-	-	-	-	-	-	-
	80	840	-	-	-	-	-	-	-	-	-	-
	80	740	-	-	-	-	-	-	-	-	-	-

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TABLE VIII-II (Continued)

Material	Time (days)	Temp. (°C)	Evolved Gas in ml/g AlH <sub>3</sub>							
			H <sub>2</sub>	N <sub>2</sub>	CO	NO	CH <sub>4</sub>	CO <sub>2</sub>	N <sub>2</sub> O	SiF <sub>4</sub>
PU-103 (Conc'l'd)	163	25*	-	-	-	-	-	-	-	-
		40*	52.7	-	-	-	-	-	-	-
		60*	575	-	-	-	-	-	-	-
		80	540	-	-	-	-	-	-	-
PU-105	29	25*	-	-	-	-	-	-	-	-
		40*	-	-	-	-	-	-	-	-
		60*	-	-	-	-	-	-	-	-
		80*	24.5	-	-	-	-	-	-	-
		70	25*	-	tr	0.1	-	tr	-	-
		40*	-	tr	tr	-	-	-	-	-
		60*	tr	tr	tr	-	-	-	-	-
		80	42.9	tr	tr	-	-	-	-	-
		80	104	-	-	-	-	-	-	-
		168	25*	-	-	-	-	-	-	-
		40*	10.2	-	-	-	-	-	-	-
		60*	86.5	-	-	-	-	-	-	-
		80*	-	-	-	-	-	-	-	-
HP	16 hr.	80	11.6	1.2	tr	tr	-	tr	-	3.3
	1	25	13.2	1.2	tr	tr	-	-	10.5	-
	40	28.9	0.5	4.3	0.3	tr	tr	0.3	> 15	0.8
	60	56.1	0.3	tr	0.2	tr	tr	-	> 15	5.0
	80	64.5	1.0	tr	-	tr	tr	0.3	> 15	0.5
										HC1
										HC1
										HC1

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TABLE VIII-II (Continued)

Material (Cont'd)	Time (days)	Temp. (°C)	Evolved Gas in ml/g AlH <sub>3</sub>							
			H <sub>2</sub>	N <sub>2</sub>	CO	NO	CH <sub>4</sub>	CO <sub>2</sub>	H <sub>2</sub> O	SiF <sub>4</sub>
HF	3	25	41.2	2.5	0.2	-	0.3	-	> 15	-
	40	28.0	0.5	7	-	tr	-	> 15	-	-
	60	92.3	-	-	tr	tr	-	> 15	-	-
	80	95.6	0.7	0.8	-	tr	0.6	> 15	-	-
7	25	120.5	-	-	tr	-	-	> 15	-	-
	40	36.3	0.5	tr	tr	tr	-	tr	2.8	-
	60	57.8	3.0	0.7	-	tr	0.3	-	6.7	-
	80	675	0.5	-	tr	-	tr	> 15	-	SiH <sub>4</sub>
8	25	437	5.6	0.1	-	0.8	0.4	-	5.0	-
	40	107	1.8	0.1	-	0.2	-	-	2.5	1.0
	60	69.3	-	tr	-	tr	0.1	-	-	-
	80	561	0.3	-	-	0.2	-	1.1	-	SiH <sub>4</sub>
15	25	272	0.2	-	0.1	0.2	-	-	3.4	0.3
	40	196	2.0	-	-	0.2	-	-	2.5	-
	60	104	0.4	-	-	tr	-	-	2.5	-
	80	346	0.3	-	-	0.2	-	-	-	HF
28	25	61	-	-	-	-	-	-	5.0	-
	40	48	-	-	-	-	-	-	0.8	-
	60	66	-	-	-	-	-	-	0.3	-
	80	590	0.4	-	-	-	-	tr	-	-

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TABLE VIII-II (Concluded)

Material HF (Conc'l'd)	Time (days)	Temp. (°C.)	Evolved Gas in ml/g AlMg <sub>3</sub>							
			H <sub>2</sub>	N <sub>2</sub>	CO	NO	CH <sub>4</sub>	CO <sub>2</sub>	N <sub>2</sub> O	SiF <sub>4</sub>
57	25	61	0.4	-	-	tr	-	-	2.0	0.8
	25	39.6	-	-	-	tr	-	-	9.3	-
40	41	tr	-	-	tr	0.4	-	tr	-	HF
40	41	-	-	tr	tr	-	-	11.4	-	HF
60	58.7	0.3	-	-	tr	0.6	-	-	-	SiH <sub>4</sub>
60	264	-	-	-	tr	0.2	-	-	-	SiH <sub>4</sub>
80	537	-	-	-	-	-	-	tr	-	-

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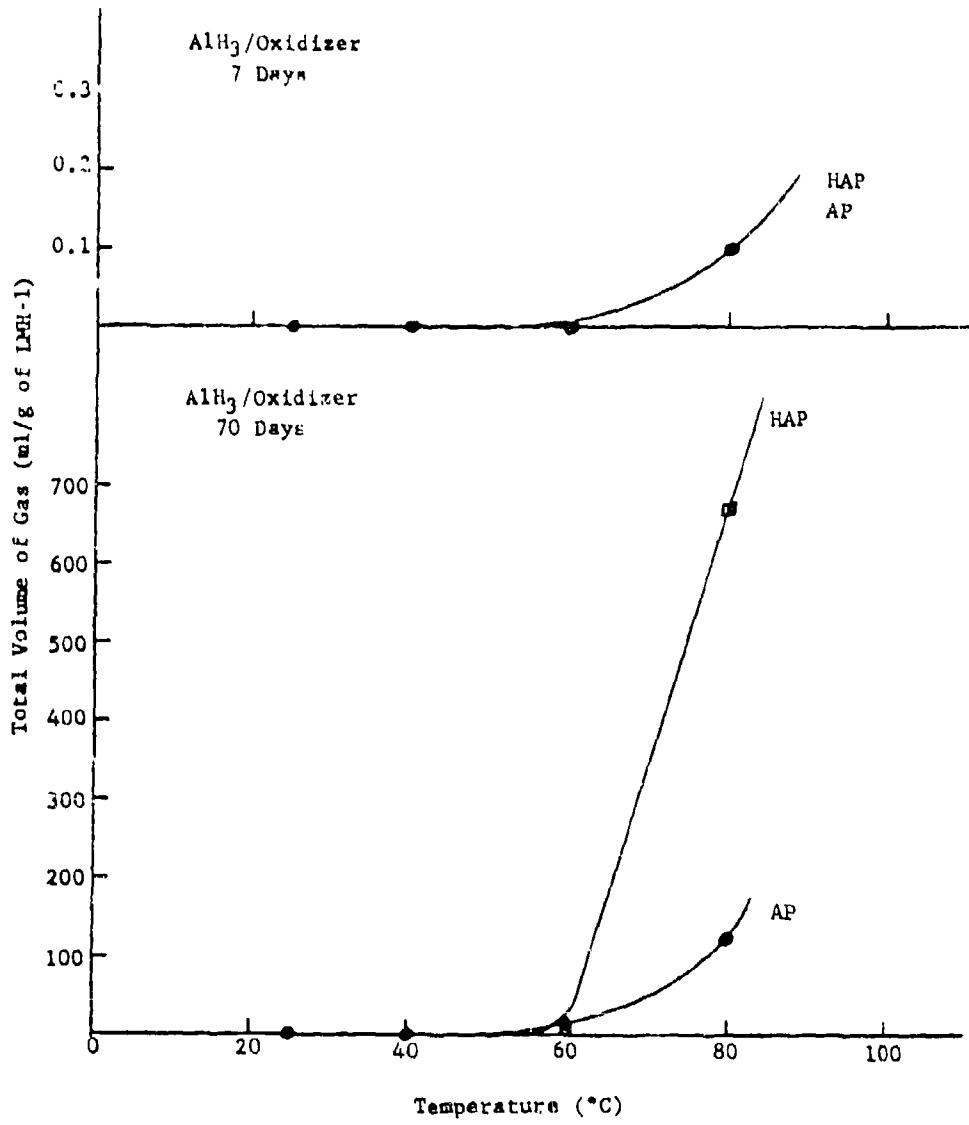


Figure VIII-2 -  $\text{AlH}_3$ /Oxidizer Compatibility

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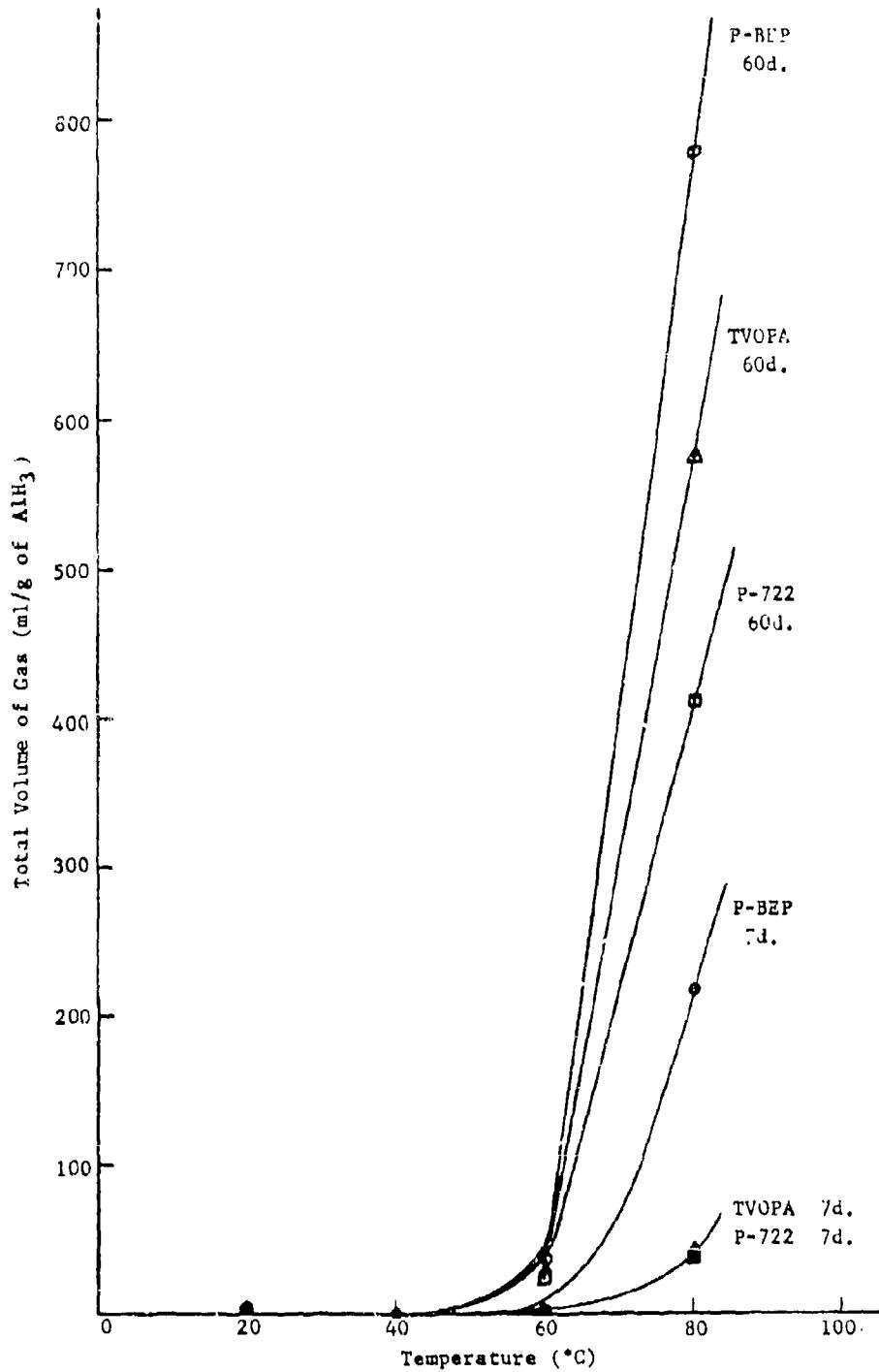


Figure VIII-3 - Total Gas Evolved from  $\text{AlH}_3/\text{NF}$  Mixtures

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Similar anomalies have been observed in a small number of cases with energetic ingredients, a situation not unexpected when working with small quantities of these materials. The other samples maintained at lower temperatures over the same time interval were all light gray in color.

(C) At 25 and 40°C and for the time periods up to 2 months, only very small quantities of gaseous decomposition products are evolved. At 60°C, hydrogen evolution increased with time for intervals greater than 15 days; TVOPA/AlH<sub>3</sub> mixtures evolved somewhat larger quantities of H<sub>2</sub> than the P-722/AlH<sub>3</sub> mixtures at this temperature. At 80°C, mixtures of each plasticizer with AlH<sub>3</sub> showed the evolution of four to five times the amount of hydrogen obtained for AlH<sub>3</sub> alone for periods of time as short as 15 days. Gaseous decomposition products other than hydrogen were also observed at 60 and 80°C, but the quantities of these products were generally small.

(C) In general, the results obtained from the P-BEP/AlH<sub>3</sub> mixtures were similar to those shown by the two NF plasticizers. At 25 and 40°C, very small quantities of gaseous decomposition products were observed for time periods up to 2 months. At 60°C, hydrogen evolution appeared to increase with increasing storage time. The data at 60 and 80°C were not always reproducible. However, since the total volume of the passivated stainless steel cells was 5 ml., the evolution of large quantities of gaseous products resulted in high internal pressures. Upon storage, this high internal pressure caused leaks to occur. As with TVOPA and P-722, the coloration of the P-BEP/AlH<sub>3</sub> mixtures indicates variations in reactivity between samples stored at the same temperature for the same period of time. Both of these factors could be the primary contributors to the variations in results which have been obtained at 60 and 80°C.

(C) These variations in the results do not detract from the fact that at 60°C, the P-BEP/AlH<sub>3</sub> mixtures evolved large quantities of hydrogen for storage times greater than 15 days. However, the total hydrogen for the mixture is less than that expected from the separate materials. At 80°C, very large quantities of other gaseous decomposition products are also observed at 60 and 80°C for all storage times.

(C) When the amount of hydrogen evolved (rather than total gas) is plotted versus temperature (Figure VIII-4) the results indicate that all three NF materials promote the decomposition of AlH<sub>3</sub> at 80°C. No increase and perhaps a decrease in the amount of hydrogen evolved is observed at 60°C and lower, over the time intervals studied.

(C) By contrast, when the quantity of gases other than hydrogen (those attributed to decomposition of the NF materials) are considered, there is little or no indication that AlH<sub>3</sub> promotes the degradation of P-BEP or of the two plasticizers.

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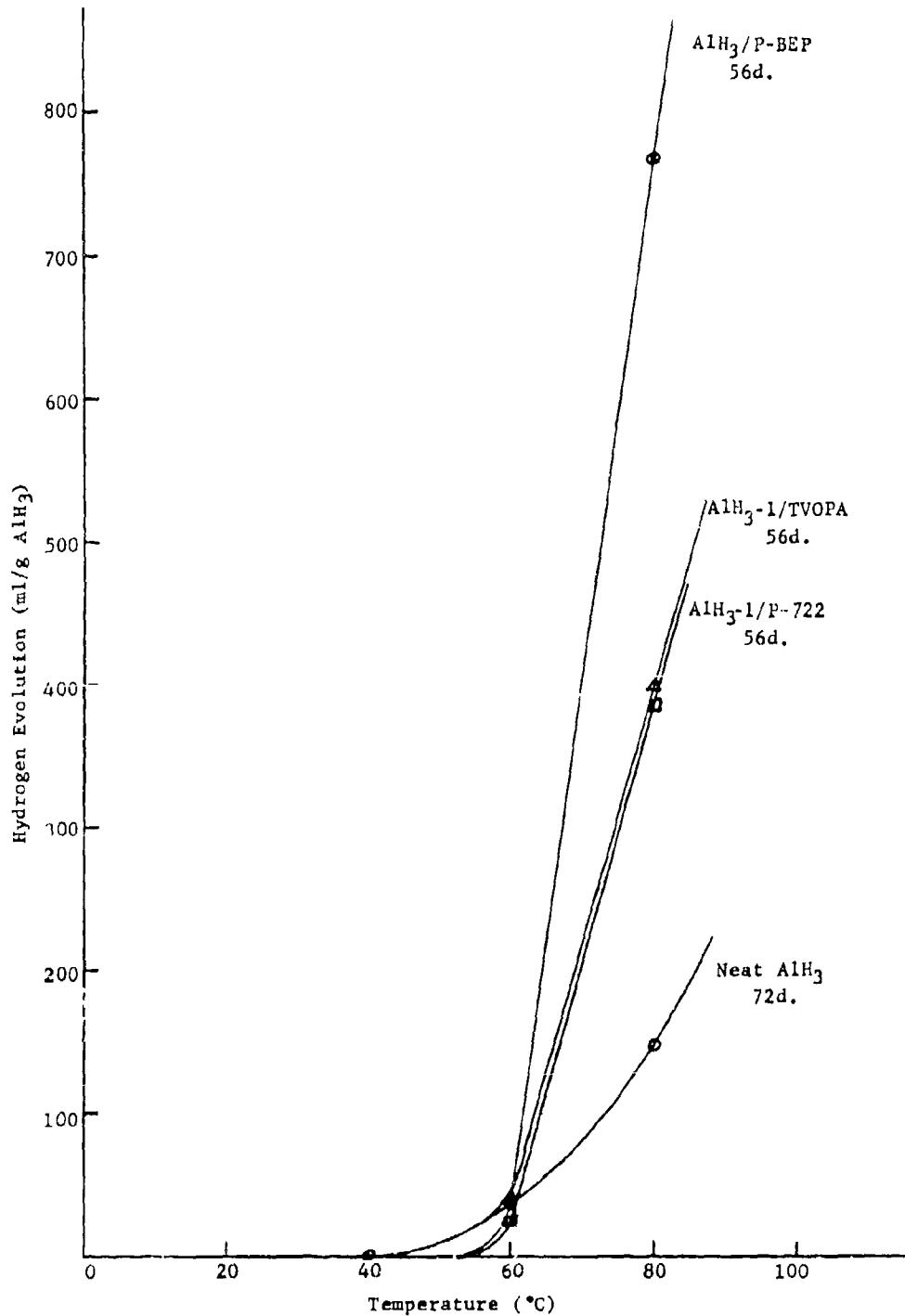


Figure VIII-4 - Hydrogen Evolved from AlH<sub>3</sub>/NF Mixtures

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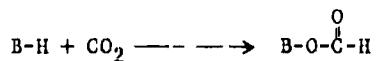
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(U)       c. Binder prepolymers: The compatibility of AlH<sub>3</sub> with two ethyl acrylate-acrylic acid binder prepolymers (PU-103 and PU-105) has been studied in glass break-seal tubes.

(C)       Neither PU-103 nor PU-105 mixtures with AlH<sub>3</sub> shows any appreciable evolution of gaseous decomposition products at temperatures up to 60°C and for storage times up to 2 months. At 80°C, the PU-103/AlH<sub>3</sub> mixtures evolved large quantities of hydrogen for all observed time periods (30 days or more). The PU-105/AlH<sub>3</sub> mixtures, at 80°C, also evolved hydrogen but to a much smaller extent than the PU-103 mixtures. Hydrogen was the only gaseous product found in greater than trace quantities for either acrylate binder at all temperatures up to 80°C and for time periods up to 6 months.

(C)       d. Hydrogen fluoride: Studies were conducted on mixtures of gaseous HF and AlH<sub>3</sub> in passivated stainless steel test cells over the temperature range of 25 to 80°C and for time intervals ranging from 16 hr. to 57 days. As anticipated, hydrogen was the principal gaseous decomposition product; however, the evolution of other gases, particularly SiF<sub>4</sub>, in appreciable quantities was somewhat surprising. The presence of SiF<sub>4</sub> has also been noted in the studies of mixtures of AlH<sub>3</sub> with TVOPA, F-722, and P-BEP, but to a much lesser extent. The presence of SiF<sub>4</sub> is attributed to silica as an impurity in the AlH<sub>3</sub>. The presence of a silicon compound, as an impurity in AlH<sub>3</sub>, is further indicated by the occasional detection of silane and fluorosilanes as gaseous products. It was also observed that the amount of SiF<sub>4</sub> evolved from these mixtures decreases with increasing reaction time indicating that SiF<sub>4</sub> undergoes further reaction with the system.

(C)       The presence of small quantities of N<sub>2</sub>, NO, N<sub>2</sub>O, and HCN can be proposed to occur as a result of the decomposition of trace impurities present in the AlH<sub>3</sub> sample. Alternatively, these gases may be present as chemically or physically absorbed species. Methane would be a logical product if trace quantities of ether solvent remains in the AlH<sub>3</sub>. Boron hydrides react with atmospheric CO<sub>2</sub> according to the reaction:



If it can be assumed that AlH<sub>3</sub> reacts in a similar manner, then the presence of small amounts of CO and CO<sub>2</sub> would be anticipated.

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C. Summary of Aluminum Hydride Studies

(C) 1. Stability: The long-term studies indicate that the Mg doped, DPA and hydrolysis treated material may have a better thermal stability than had been previously reported by Dow. Our results indicate approximately 3% decomposition after 72 days at 60°C and approximately 10-14% decomposition at 80°C for the same time period.

(C) Mass spectrometric data indicate the presence of unstable species in AlH<sub>3</sub> and that the source of instabilities may be removed by utilizing a thermal cycle.

(C) 2. Oxidizer compatibility: Neither AP nor HAP underwent any appreciable reaction with AlH<sub>3</sub> for time intervals up to 28 days at 25, 40 or 60°C. After 70 days, AP produced no gaseous decomposition products at 25 and 40°C. At 60°C, hydrogen was evolved from the AP/AlH<sub>3</sub> mixture. The data for HAP were very similar to those for AP after 70 days, except that only trace quantities of hydrogen were observed at 60°C. At 80°C, hydrogen was evolved from both the AP/AlH<sub>3</sub> and HAP/AlH<sub>3</sub> mixtures for all time periods. AP/AlH<sub>3</sub> consistently evolved less hydrogen than HAP/AlH<sub>3</sub>; however, neither mixture evolved appreciable quantities at any temperature studied for time periods up to 28 days. After 70 days at 80°C, AP mixtures produced considerably less hydrogen than HAP mixtures but the quantities from both oxidizers were appreciable.

(C) 3. NF compatibility: TVOPA and P-722 appeared to be approximately the same with respect to their compatibility with AlH<sub>3</sub>. Neither plasticizer promoted the decomposition of AlH<sub>3</sub> as indicated by H<sub>2</sub> evolution, or underwent dissociation to any significant extent at 25 or 40°C for time periods up to 56 days. After 56 days at 60°C, both the AlH<sub>3</sub>/TVOPA and AlH<sub>3</sub>/P-722 mixtures showed hydrogen as the principal gaseous decomposition product, and the mixtures evolved more hydrogen than is expected from AlH<sub>3</sub> alone. At 80°C for the same time interval, both mixtures evolved large quantities of hydrogen and small amounts of numerous gaseous products which result from the decomposition of the plasticizer.

(C) At 25 and 40°C, the AlH<sub>3</sub>/P-BEP mixture evolved only small quantities of gaseous products for time intervals up to 56 days. At 60°C, the total gas evolved was significantly greater with hydrogen as the principal product. After 56 days at 80°C, significantly larger quantities of gases were evolved, and again hydrogen was the main product.

(C) 4. Acrylate binder compatibility: The PU-103/AlH<sub>3</sub> mixture produced only small quantities of hydrogen at temperatures up to 60°C for time intervals of 70 days, and at 25 and 40°C after 163 days. For the longer time period, significant amounts of hydrogen (50 ml/g AlH<sub>3</sub>) were evolved

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at 60°C. The samples maintained at 80°C showed the evolution of large quantities of hydrogen for time intervals ranging from 30 to 163 days. For the PU-103/AlH<sub>3</sub> mixtures, very little gas evolution was observed for temperatures up to 60°C and time intervals ranging from 29 to 168 days. The lone exception was at 60°C for the 168-day time interval when approximately 10 ml. of H<sub>2</sub> was evolved. At 80°C, significant amounts of hydrogen were evolved at all reported time intervals.

(C) 5. HF compatibility: As expected, HF and AlH<sub>3</sub> react easily, yielding hydrogen and (presumably) AlF<sub>3</sub>. HF indigenous in oxidizers such as P-BEP is thus capable of reacting with AlH<sub>3</sub>. This factor is a serious potential problem; data on PBEP-AlH<sub>3</sub> compatibility somewhat inexplicably do not indicate that HF-AlH<sub>3</sub> reaction is a problem.

D. References

(U) 1. Dow Chemical Company, Report No. AR-3Q-63, Contract No. AF04(611)-7554.

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IX.

## PROPELLANT STABILIZERS

### A. Introduction

Numerous investigations, including studies at this laboratory, have indicated the need for stabilizing solid propellants against the detrimental effects of the various decomposition species produced by propellant ingredients under processing and storage conditions. The following are included among the simpler materials identified: HF, HClO<sub>4</sub>, H<sub>2</sub>, H<sub>2</sub>O, HCN, CO, N<sub>2</sub>O, N<sub>2</sub>, and CO<sub>2</sub>. The first three are primary decomposition species from NF binder, oxidizer, and hydride fuel, respectively. The other species usually result from continued decomposition of the propellant components or reaction of the latter with HF and/or the oxidizer. These studies and investigations at Lockheed have noted an apparent mutual stabilization effect among the ingredients of the advanced propellant, i.e., the ingredients together show greater stability than in their neat condition. Hence, any method for improving advanced propellant processing and aging characteristics must not disrupt the mutual stability enhancement mechanism. In other words, before a propellant can be stabilized, logically, the detrimental effect must be identified. These effects, in turn, will depend on the nature of the propellant. For example, stabilization requirements for a propellant containing HF ingredient and hydride fuel will be significantly more complicated than an NF plasticized conventional propellant.

Historically, this phase of the program was initiated to develop stabilization methods for ingredients, then to apply the stabilization method to various combinations of components so as to identify situations of optimum utility (i.e., a given method may be effective in a nonhydride propellant but of no consequence in a more conventional formulation). The overall approach was, therefore, synthetic rather than analytical.

In attacking the simplest situation, i.e., decomposition species, a plausible method for stabilizing propellants against these reactive materials is to absorb them (HF, HClO<sub>4</sub>, etc.) via appropriate scavengers. HF evolution from NF materials was a major storage problem at the time this phase of the program was initiated; hence, primary efforts during the early stages of this phase were addressed to the problem of devising scavenger methods for the removal of HF as a reactive species in propellant systems.

### B. Approach--Scavenger Development

The first step in the scavenger development effort was the selection and evaluation of materials capable of absorbing either by reaction or

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adduct formation, the reactive material (in this case HF) formed by decomposition of the ingredients of a propellant during processing and/or storage. As a second development step, the compatibility of such materials with other propellant components and processes must be determined. Performance in propellant formulations is the final demonstration point. Within the framework of the level of effort of this phase of the program, it was possible to make considerable progress through steps one and two and to recommend materials for formulation evaluation.

Criteria for HF scavenger selection are listed below:

The candidate must give rapid but not excessively exothermic reaction with HF.

Its physical properties must be compatible with propellant properties, i.e., volatility sufficiently low so as not to diffuse through and from the propellant during storage and a boiling point high enough to withstand processing conditions (e.g., no lower than 60°C). Solubility in the binder is desirable.

The scavenger must be chemically compatible with propellant ingredients: dehydrofluorination must not be catalyzed by the scavenger nor should any side reactions occur to the detriment of overall propellant stability (both chemical and structural).

Weight and volume limitations must be met; the scavenger must have a high HF absorption capacity (moles HF absorbed/mole of scavenger).

The cost of the material should be low.

Scavenger action towards other degradation products (e.g., H<sub>2</sub>O, HClO<sub>4</sub>) would be a bonus effect.

The results of the scavenger action towards HF must not result in the formation of new species detrimental to propellant storage. For this reason, compounds undergoing addition reaction or adduct formation should be given prime consideration.

The initial phase of the program was designed to identify HF-absorbers, that is, materials capable of taking up HF rapidly to give stable adducts or addition compounds. Such materials, however, are not HF-scavengers per se. A differentiation must be made, since a scavenger must be an HF-absorber which will operate successfully under conditions prevalent in a propellant matrix, i.e., diffusion controlled reactions in addition to meeting the other requirements. Hence, the experimental procedure must entail several phases. Materials were selected which are known to react

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with HF and which, intuitively, appeared to give the desired compatibility behavior with other propellant ingredients. The ultimate utility of a given scavenger system will depend on its performance in an actual propellant formulation. However, economy and logic demand that each candidate system be evaluated first according to parameters stated above. With this in mind the following evaluation scheme was devised:

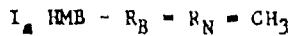
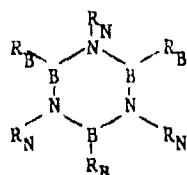
Material selection was based on indications from the literature of desired reaction rate and direction with HF and compatibility with other materials.

HF reaction screening studies entailed determination of the rate and nature of reaction with HF. Here, the simplest system was used: various pressures of HF in contact with the candidate. Products (both residue and gaseous) were analyzed by a combination of methods (IR, NMR, mass spectrometry). The effect of low pressures on the reaction was determined, since the actual pressure of HF in a propellant will be low. From the nature and rate of reaction it has been possible to eliminate certain materials at this early stage in the program.

## C. Data and Results

The bulk of the work centered on screening several classes of compounds with HF and P-BEP.

1. Borazine class: Compounds containing the borazine ring are



reported to form adducts with halogen acids (Ref. 1), though HF was not mentioned specifically. To thoroughly characterize the borazine-HF reaction system and its products, three compounds were examined: hexamethylborazine (HMB), I where  $R_B = R_N = -CH_3$ , B-trichlorotrimethylborazine (TCMB), I where  $R_B = Cl$  and  $R_N = CH_3$ , and B-trichloroborazine (TCB) where  $R_B = Cl$  and  $R_N = H$ . The latter two were examined primarily as aids for interpretation of reaction product data from the HMB-HF reaction.

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(U) The HF-HMB data are summarized in Table IX-I. HF is taken up rapidly and a stable adduct is formed where the pressure of the gas applied represents a stoichiometric ratio of 3:1 HF to substrate. Excessively high HF pressure, however, led to HMB degradation. The HMB-HF adduct can be isolated and stored; it has a melting point of 138-139°C and its decomposition behavior is indicative of salt dissociation as will be described later.

(U) Where chlorine is the boron substituent, HF readily undergoes a substitution reaction with the borazine compound in which the chlorine is replaced by fluorine and HCl is generated. No CF bond formation has been observed in any of the reactions (Table IX-II).

(U) The mass spectral cracking pattern for the product of the reaction of HMB with HF is shown in Figure IX-1. These data have been corrected for the air leak which occurs upon insertion of the probe. It cannot be corrected for the accompanying increase in the water peak ( $m/e$  18). Thus, while the most intense peak in the spectrum is shown as being  $m/e$  18, this is not a true representation of the actual quantity of water absorbed in the sample.

(U) HMB sublimes very readily under vacuum and studies of this material with the mass spectrometer have shown that, at the normal pressure of the instrument ( $10^{-7}$  torr), the mass spectrum must be obtained within 1-2 min. after insertion or the sample will be sublimed from the crucible.

(U) With this background information in mind, the cracking pattern indicates very strongly that adduct formation does occur. As anticipated, a molecular ion for the adduct was not observed; however, mass values were observed;  $m/e$  20 (HF) and the higher  $m/e$  values, corresponding to HMB. Since this sample was thoroughly evacuated these species would have disappeared if the material were a simple mixture rather than an adduct. In addition, no methyl group fluorination is indicated due to the lack of peaks at mass values greater than 165 ( $HMB^+$ ), particularly at  $m/e$  183, 201, etc., which would be indicative of  $-CH_2F$  groups present in the HMB. Aside from water and HF, all other mass values shown in Figure IX-1 can be attributed the fragmentation of HMB in the ion beam. Hence, it was concluded that the HMB-HF adduct is indeed a salt.

(C) As the next step in the evaluation of HMB as a possible HF scavenger, this material was combined with P-BEP and subjected to conditions under which the polymer is known to decompose.

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TABLE IX-I

HMB-HF REACTION DATA

<u>Material/System</u>	<u>Conditions</u> <u>Temp./Time/Pressure</u> <u>(°C-days/atm)</u>	<u>Rate</u> <u>of</u> <u>Uptake</u>	<u>Gas Analyses</u> <u>(ml. gas/g substrate)</u>	<u>Residue Analysis</u>
HMB-HF	25/1/1	Rapid	10.0-H <sub>2</sub> ; 7.3-CH <sub>4</sub> , 0.3-N <sub>2</sub>	Turned from white solid to amber liquid
HMB-HF	25/4 hr/0.16	Rapid	tr-H <sub>2</sub> ; nH <sub>1</sub>	HF taken up rapidly; residue-white solid m.p. 138-139; MS- adduct, no fluorination or decomposition of HMB
Reaction and results reproduced in triplicate				
HMB-HF	25/1/0.03	Rapid	None	Mixture of adduct and HMB
HMB-HF	25/1/0.01	Rapid	None	Mixture of adduct and HMB

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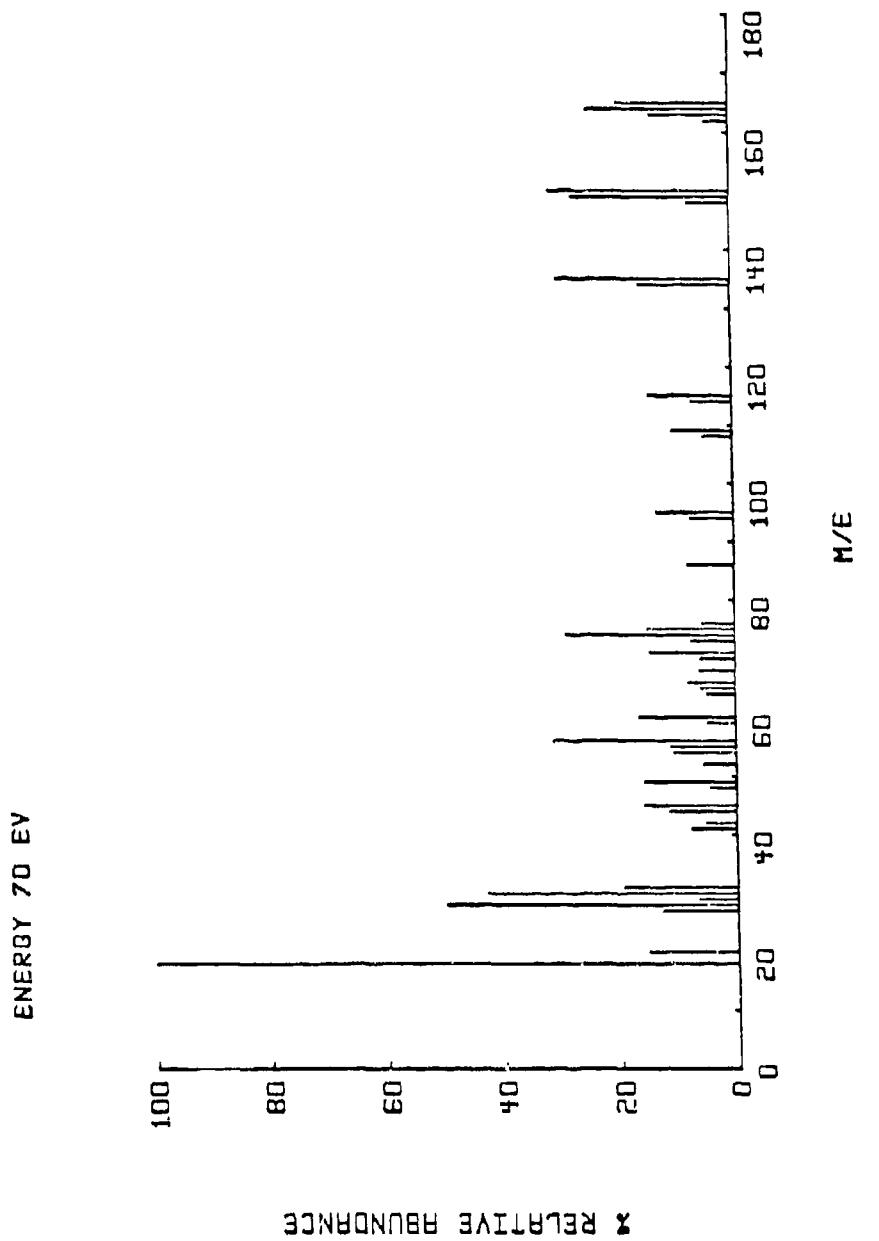
TABLE IX-II  
CHLOROBORAZINE HF INTERACTION DATA

<u>Material/System</u>	<u>Conditions</u> <u>Temp/Time/Pressure</u> <u>(°C/days/atm)</u>	<u>Rate</u> <u>of</u> <u>Uptake*</u>	<u>Gas Analyses</u> <u>(ml. gas/k. substrate)</u>	<u>Residue Analysis</u>
TGBB-HF	25/18 hr/0.16	Rapid	2.6-H <sub>2</sub>	TFBB-15.1%; difluoro-chloromethylborazine-3.3%; fluorodichloromethylborazine-1.5%; HCl-42%; CH <sub>3</sub> NHBF <sub>3</sub> -15.8%; HF-1.1%; TGBB-0.4%; CH <sub>3</sub> NH <sub>2</sub> -20.8%; Cl replacement by F and ring cleavage occurred.
TCE-HF	25/18 hr/0.16	Rapid	2.2-SiF <sub>4</sub>	Mono and difluoro substitution for Cl. Same trend as above.

\* Relative to HFB.

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Table IX-III lists the data from a series of HMB-P-BEP runs on the crude polymer in both metal and glass systems\* at elevated temperatures (60 and 80°C) for 34 days. HMB appears to stabilize P-BEP by absorbing the HF expected to be evolved under the test conditions. Under similar conditions (55-70°C) refined P-BEP evolved total amounts of gas (excluding CH<sub>2</sub>Cl<sub>2</sub> which is usually present) ranging from 11.2-14.2 ml. gas/g of P-BEP (containing 2.0-6.5 ml. HF/g P-BEP). When HMB (1:4 wt/g ratio) is added to crude P-BEP, only once in seven runs was any fluorine containing species observed, and the total amount of gas evolved in all cases was considerably less than the reference samples. The observation of fluorine species in one of the runs may be due to poor mixing of that specific sample.

(C) The combination of P-BEP and AlH<sub>3</sub> shows improved stability compared to the two materials in their neat condition. This trend can be seen in Figure IX-2 where the results of decomposition studies of P-BEP at a number of different temperatures are plotted as a function of time. The P-BEP/AlH<sub>3</sub> combinations at both 40 and 60°C fall below the gas-evolution curves for the neat polymer, indicating an in situ stabilization effect between the components. Studies were undertaken to determine the minimum effective concentration of HMB required to stabilize the polymer relative to this in situ effect. The results of this series run at 60°C (65-day period) show good reproducibility and are plotted in Figure IX-3. The 4:1 ratio values have been extrapolated to the 65-day period and fit well on the plot. Gas evolution from P-BEP/AlH<sub>3</sub> (1:1) at 60°C would fall in the 35-40 cc/g of polymer range; P-BEP alone would be in a range higher than the latter when extrapolated to the 65-day period.

(C) As would be expected, the degree of stabilization is directly proportional to the amount of HMB present; but even at a 20:1 ratio of P-BEP to HMB, gas evolution is significantly less than that for polymer and hydride combination without the additive. The incorporation of HMB into the P-BEP/AlH<sub>3</sub> mixture, when put in context of this type of data treatment, leads to a threefold improvement over the hydride-NF alone though it is still not as effective as the polymer-HMB would be without hydride. Hence the addition of HMB to the NF-hydride combination does not appear to adversely alter the in situ stabilization interaction but, in fact, improve it. Figure IX-4 summarizes the stability behaviors of several ingredient combinations and, once again, the stabilizing effect of HMB is demonstrated.

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\* Glass systems were used because of (1) experimental ease, (2) if scavengers were not effective SiF<sub>4</sub> would be formed and is very easily detected, and (3) glass provides a rigorous test system for comparing the effectiveness of scavengers.

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TABLE IX-III

HMB - P-BEP REACTION DATA

<u>Material/System</u>	<u>Conditions</u>	<u>Gas Analysis</u> (ml. Gas/g. substrate)	<u>Apparatus Construction</u>
HMB - P-BEP* (25 mg. - 100 mg.)	60/5 nil	nil	Metal system
HMB - P-BEP (25 mg. - 100 mg.)	80/5 nil	nil	Metal system
HMB - P-BEP (25 mg. - 100 mg.)	60/34 No H <sub>2</sub> ; no F materials; 0.5-HCN; 0.2-CH <sub>4</sub>	No H <sub>2</sub> ; no F materials; 0.5-HCN; 0.2-CH <sub>4</sub>	Glass breakseal
HMB - P-BEP (25 mg. - 100 mg.)	60/34 No H <sub>2</sub> ; no F species; 0.7-HCN	No H <sub>2</sub> ; no F species; 0.7-HCN	Glass breakseal
HMB - P-BEP (25 mg. - 100 mg.)	60/34 No H <sub>2</sub> ; 3.0-SiF <sub>4</sub> ; 0.5-HCN	No H <sub>2</sub> ; 3.0-SiF <sub>4</sub> ; 0.5-HCN	Glass breakseal
HMB - P-BEP (25 mg. - 100 mg.)	80/34 No H <sub>2</sub> ; no F species; 0.9-CH <sub>4</sub> ; 0.6-CO <sub>2</sub> ; 0.3-CO; 0.3-HCN	No H <sub>2</sub> ; no F species; 0.9-CH <sub>4</sub> ; 0.6-CO <sub>2</sub> ; 0.3-CO; 0.3-HCN	Glass breakseal
HMB - P-BEP (25 mg. - 100 mg.)	80/34 No H <sub>2</sub> ; no F species; 1.9-CH <sub>4</sub> ; 0.5-CH <sub>2</sub> ; 0.4-CO	No H <sub>2</sub> ; no F species; 1.9-CH <sub>4</sub> ; 0.5-CH <sub>2</sub> ; 0.4-CO	Glass breakseal
P-BEP	55/35 5.4-N <sub>2</sub> ; 0.9-CO; 0.4-CO <sub>2</sub> ; 0.1-N <sub>2</sub> O; 2.0-HF; 2.6-HCN (2.8-CH <sub>2</sub> C <sub>12</sub> ) <u>Total 11.4</u>	5.4-N <sub>2</sub> ; 0.9-CO; 0.4-CO <sub>2</sub> ; 0.1-N <sub>2</sub> O; 2.0-HF; 2.6-HCN (2.8-CH <sub>2</sub> C <sub>12</sub> ) <u>Total 11.4</u>	Metal, P-BEP purified
P-BEP	70/35 3.5-N <sub>2</sub> ; 2.3-CO; 1.1-CO <sub>2</sub> ; 0.1-N <sub>2</sub> O; t-H <sub>2</sub> ; t-CH <sub>4</sub> ; 6.5-HF; 0.7-HCN (2.8-CH <sub>2</sub> C <sub>12</sub> ) <u>Total 14.2</u>	3.5-N <sub>2</sub> ; 2.3-CO; 1.1-CO <sub>2</sub> ; 0.1-N <sub>2</sub> O; t-H <sub>2</sub> ; t-CH <sub>4</sub> ; 6.5-HF; 0.7-HCN (2.8-CH <sub>2</sub> C <sub>12</sub> ) <u>Total 14.2</u>	Metal, P-BEP purified

\* Crude P-BEP.

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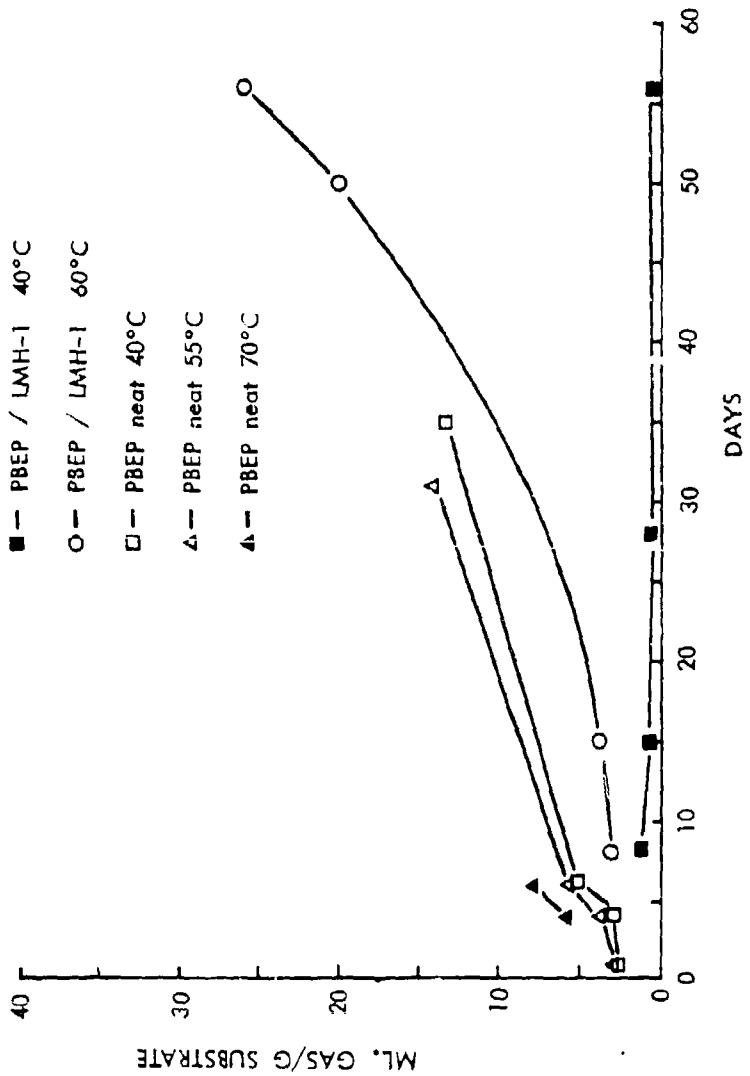


Figure IX-2 - Comparative Gas Evolution NF AlH<sub>3</sub> Systems

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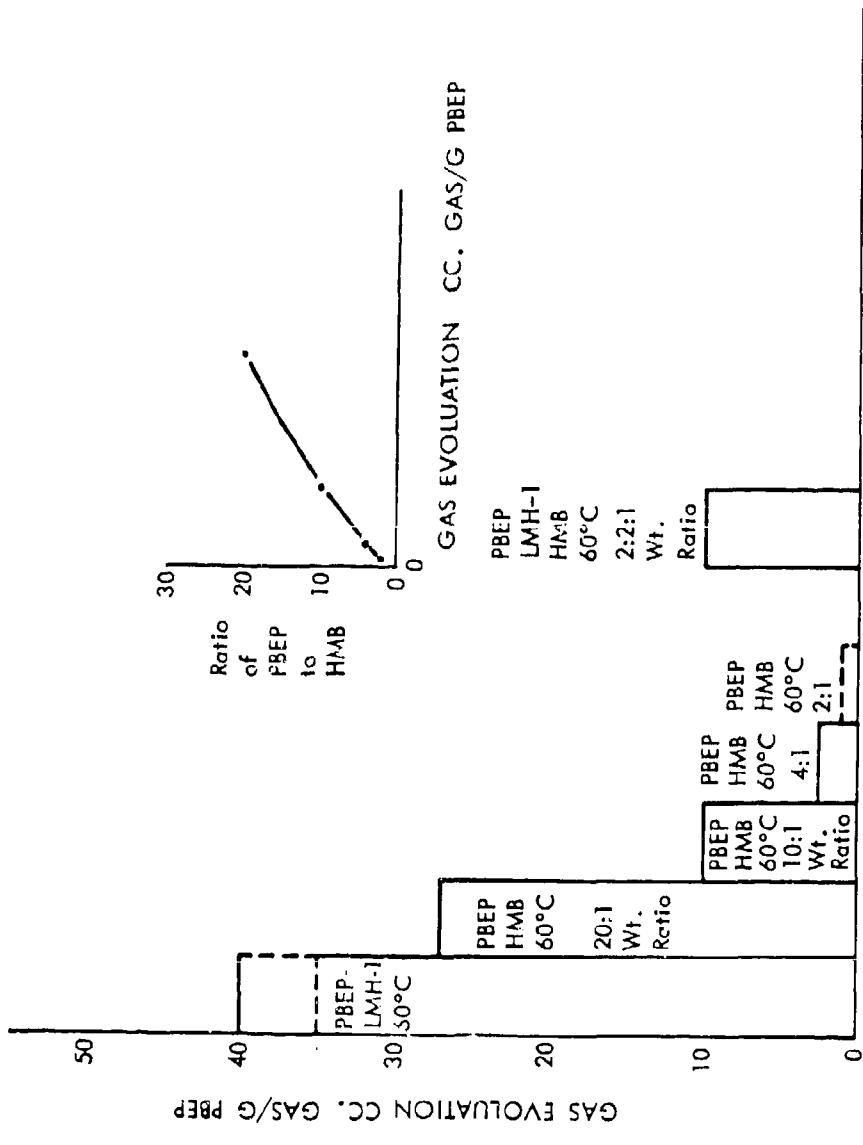
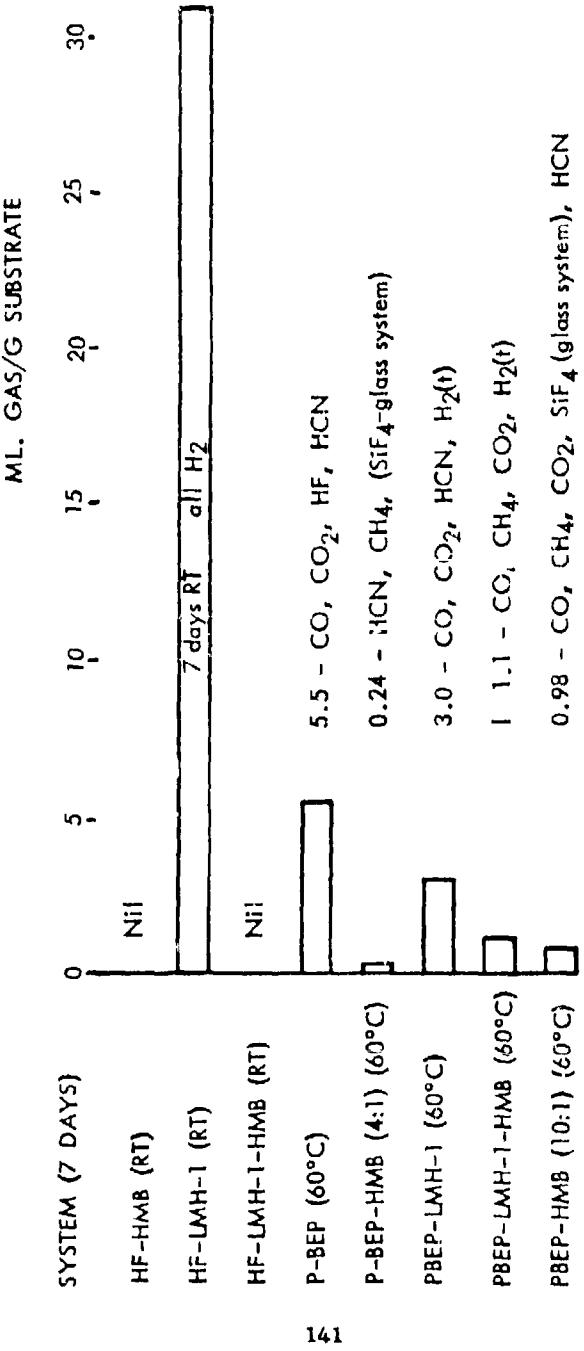


Figure IX-3 - Effect of HMB Concentration on Gas Evolution From P-BEP and P-BEP/AIH<sub>3</sub> Mixtures at 60°C in 65-Day Period. 10:1 Values are Derived at 7 and 30 Days; 4:1 from 7 Days of Data; 2:1 Value is Extrapolated (see inset).



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Figure IX-4 - Comparative Stabilities of Hydride-NF-HMB Combinations

(C) The results of long term compatibility studies on mixtures of AlH<sub>3</sub> and NF materials with HMB are presented in Table IX-IV. The 60°C data for the P-BEP/AlH<sub>3</sub>/HMB and P-BEP/AlLi<sub>3</sub> systems are particularly revealing. In both cases, both hydrogen and HCN are evolved in significant quantities, the former coming from the thermal decomposition of AlH<sub>3</sub> and the latter from P-BEP. In both cases, the average amounts of these gases are about the same, indicating relatively similar stabilities at that temperature. However, the amount of SiF<sub>4</sub> liberated in the HMB containing system is significantly lower than that in the mixture without HMB. These results agree with the results of the short-term evaluation studies which indicated HMB to be an effective HF scavenger at 60°C.

(U) The 40°C data indicate little difference in degree of degradation due to the presence of HMB. The degradation is slight and it is questionable whether the analytical techniques employed are sufficiently sensitive to detect changes in the minute amounts of gas evolved at these temperatures over these relatively short time periods. Similar observations are noted in the P-722 systems (Table IX-V).

(C) Thus far, HMB has been shown to be compatible with P-BEP (in that the P-BEP decomposition rate in HMB mixtures is slower, much slower than the neat polymer); HMB is compatible with the hydride and does not adversely affect any stabilization effects manifest in the AlH<sub>3</sub>/NF system and finally HMB does not undergo gas evolution reaction with isocyanate. The latter point introduces another important area for evaluation, that is, the effect of HMB on the cure properties of the propellant. The fact that no gas evolution is noted from a mixture of HMB and isocyanate does not preclude the possibility of condensation (nongas evolving) reaction taking place. With this in mind, several solution studies were undertaken.

(U) HMB was added to a solution of phenylisocyanate in carbon tetrachloride and stirred at room temperature. The isocyanate concentration was monitored by IR (4.46  $\mu$ ) and no change was noted in a 4-day period. However, after 5 days the solution became progressively cloudy and a precipitate formed. Isolation of the latter and analysis by IR and DTA showed it to be diphenylurea. An examination of the records relative to this experiment showed that only after the reaction flask had been removed from the dry bag (nitrogen atmosphere) did the solution cloud of the precipitate form. The experiment was repeated. This time the CCl<sub>4</sub>/phenylisocyanate/HMB was kept exclusively in the nitrogen environment. A similar solution was prepared into which a micro quantity of water was introduced. The diphenylurea formed only in the latter case. The HMB used for these runs was handled routinely in either dry box or dry bag; hence, the formation of urea is due to atmospheric moisture and not the hygroscopicity of the HMB. No additional evidence had been found to the conclusion of the program to change the previous conviction that HMB is compatible with P-BEP and the isocyanate functionality.

TABLE IX-IV

COMPATIBILITY OF P-BEP AND  $\text{AlF}_3$  WITH AND WITHOUT HMB

System	Temp. (°C.)	Time (Days)	Ml. of Gas/Gram of P-BEP							
			$\text{H}_2$	$\text{N}_2$	$\text{O}_2$	$\text{CO}$	$\text{NO}$	$\text{CH}_4$	$\text{CO}_2$	$\text{N}_2\text{O}$
<b>P-BEP/LMH-1/HMB</b>										
P-BEP = 50 mg.	25	119	--	5.1	4.4	0.7	--	--	--	--
LMH-1 = 100 mg.	25	119	--	--	--	--	--	--	--	--
HMB = 2.5 mg.	25	119	--	--	--	--	--	--	--	--
P-BEP/LMH-1	25	57	--	--	--	--	--	--	--	5.7
P-BEP/LMH-1	25	57	--	--	--	--	--	--	--	7.0
P-BEP/LMH-1	25	157	--	--	--	--	--	--	--	4.0
P-BEP/LMH-1/HMB	40	119	--	--	--	--	--	--	--	5.3
P-BEP/LMH-1/HMB	40	119	tr	--	--	tr	--	--	1.4	1.0
P-BEP = 50 mg.	40	119	--	--	--	--	tr	tr	--	--
LMH-1 = 100 mg.	40	119	tr	--	--	tr	--	tr	--	--
HMB = 2.5 mg.	40	119	tr	--	--	tr	--	tr	--	--
P-BEP/LMH-1	40	119	tr	--	--	tr	--	tr	--	1.4
P-BEP/LMH-1	40	57	--	--	--	--	--	--	--	--
P-BEP/LMH-1/HMB	60	64	8.7	0.9	--	0.3	--	0.6	1.7	4.4
P-BEP = 50 mg.	60	64	17.4	0.9	--	0.3	--	0.3	0.9	4.3
LMH-1 = 50 mg.	60	64	69.9	1.4	--	3.2	--	0.9	2.0	2.3
HMB = 10 mg.	60	64	31.9	0.9	--	0.3	--	0.3	0.9	2.6
P-BEP/LMH-1	60	57	40.2	1.1	--	tr	--	--	0.2	4.0
P-BEP/LMH-1	60	57	5.0	1.1	--	--	--	--	3.0	11.2
										11.4

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TABLE IX-V  
COMPATIBILITY OF P-722 AND  $\text{AlH}_3$  WITH AND WITHOUT HFB

System	Temp. (°C)	Time (Days)	Ml. of Gas/Gram of P-722			
			H <sub>2</sub>	CO	CO <sub>2</sub>	HCN
SiF <sub>4</sub>						
P-722/LMH-1/HFB	25	119	--	--	--	--
P-722 = 50 mg.	25	119	--	--	--	--
LMH-1 = 100 mg.	25	119	--	--	--	--
HFB = 2.5 mg.	25	119	--	--	--	--
P-722/LMH-1	25	119	--	--	--	--
P-722 = 50 mg.	25	137	--	--	--	--
LMH-1 = 100 mg.	25	134	--	--	--	--
HFB = 2.5 mg.	25	119	--	--	--	--
P-722/LMH-1	40	119	tr	--	--	--
P-722 = 50 mg.	40	119	--	tr	--	--
LMH-1 = 100 mg.	40	119	tr	--	--	--
HFB = 2.5 mg.	40	119	--	0.4	--	--
	40	119	tr	tr	--	--
					Trace acetone	Trace ethylacetate
					--	--

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In summary, the salient points concerning HMB and the NF/hydride system are as follows:

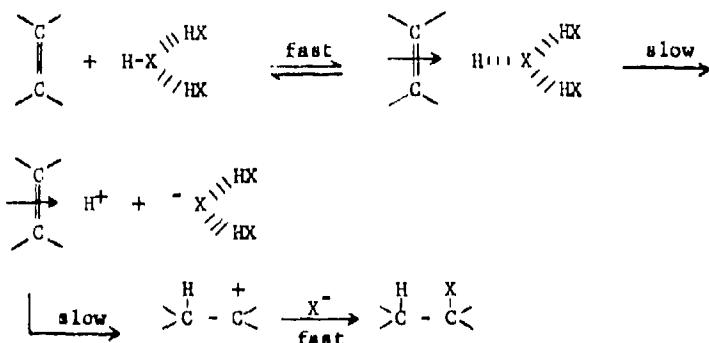
a. HMB is hydroscopic; however, it appears to be significantly less sensitive to moisture contamination than are the isocyanate curing agents.

b. Studies to date indicate that HMB is an effective HF scavenger and is effective in reducing the gas evolution rate of P-BEP.

c. Addition of HMB to a P-BEP/AlH<sub>3</sub> mixture results in a similar reduction in gas evolution rate.

d. No evidence has been obtained to date to indicate that HMB undergoes side reactions adverse to propellant cure or storage.

2. Unsaturated compounds: Hydrogen halides are known to interact with  $\pi$  as well as  $n$  donors. The addition is proposed to occur through formation of a  $\pi$  complex (fast step) followed by ionization of the hydrogen halide, carbonium ion formation and then addition of halide ion (Ref. 2).



Anhydrous HF is reported to form 1:1 complexes with aromatic substances. Hence, a series of aromatic and unsaturated materials were screened with HF to determine whether indeed such reactions would occur with HF under conditions necessary for scavenger activity. The data are tabulated in Table IX-VI. In general, all those materials tested absorbed HF as indicated by the decrease in pressure observed during the course of the experiments. However, no fluorine containing products were ever isolated; the aromatics were recovered unchanged (HF was given off from these materials as indicated by the etching of glass capillary tubes, etc.). These data are in accord with the addition mechanism cited above. Under the test conditions, HF forms the equilibrium complex with the  $\pi$  bond and conditions are not such

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TABLE IX-VI

HF-M COMPOUND REACTION DATA

<u>Material/System</u>	<u>Conditions</u>	<u>Rate</u>	<u>Gas Analysis</u>	<u>Residue Analysis</u>
	<u>Temp/Time/Pressure</u> (°C/days/atm)	<u>Uptake</u>	<u>(ml. gas/g substrate)</u>	
DPA-HF	25/21/0.16	Moderate	8.6-H <sub>2</sub> ; 1.7-HF	Light yellow solid remaining; m.p. - 58.5-59.5; mass spec. HF + DPA; no P addition.
	25/3/1	Moderate	132-H <sub>2</sub> ; 0.1-CH <sub>4</sub>	Black solid; melting range, 172-197; fluorinated and de- graded starting material.
TPBT-HF	25/3/0.16	Moderate to slow	26.4-H <sub>2</sub>	Unstable complex formed; slight shift in melting point.
HNO-HF	25/18/0.16	Moderate to rapid	9.2-H <sub>2</sub>	Black liquid; possible C-F for- mation; to be reexamined.
HDY-HF	25/18/0.16	Moderate		Unstable complex; to be re- examined.
TPE-HF	25/3/0.16	Moderate to slow	7.9-H <sub>2</sub>	Unstable complex formed; slight shift in melting point.
COT-HF	25/18/0.16	Moderate	2.6-H <sub>2</sub> ; 5.0-HF	Partial HR absorption only. Products are mixtures of un- saturated hydrocarbons resulting from rearrangement, cleavage, and homopolymerization of COT; no evidence of HF addition to double bonds.

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as to allow progression beyond this point. The etching of glass by the complex sample is indicative of a shift in equilibrium to the left caused by the presence of a material more reactive towards HF (glass) than the unsaturated substrate. The aromatic substituted olefins and acetylenes were more stable towards HF than were the purely hydrocarbon unsaturates. There is a tendency for the latter materials to undergo acid-catalyzed cleavage and rearrangements (e.g., COT). This effect is in agreement with observations noted in the literature (Ref. 3).

(C) To determine whether the complexes are sufficiently strong to stabilize a propellant, mixtures of P-BEP and several aromatic unsaturates were stored at 80°C for a week (Table IX-VII). Figure IX-5 is a plot of the range of gas evolution values for P-BEP between 4 and 7 days over a temperature range of 40-70°C. The gas evolution values for P-BEP/unsaturate samples (at 80°C) falls below the envelope, even below that for 40°C. No HF or fluorine containing species were found in the gas phase. These results suggest that P-BEP is being stabilized by the additives. Indeed, other workers have reported the presence of COT to stabilize hydride-NF propellants relative to formulations lacking the unsaturated additives. The nature of this stabilization interaction is unknown. Definition is required of AlH<sub>3</sub> reactivity with NF and unsaturated species before a stabilization mechanism can be formulated.

(U) 3. Miscellaneous studies: Initial experiments were run to determine the possible use of HMB as a perchloric acid scavenger. Samples containing equal weights of HMB and HAP were prepared by recrystallization from ether and stored in a dry bag for 30 days. Direct-inlet mass spectral analysis showed initial peaks (ambient temperature) attributable to ether and HMB as expected. After 20 min. at 45°C the spectrum consisted only of background. Continued heating of the sample to 70°C led to the evolution of more ether. Beyond this temperature, peaks associated with HONH<sub>2</sub>, HClO<sub>4</sub>, HMB, and ether were observed. Above 90°C, m/e 33 (HONH<sub>2</sub>) increased much more rapidly than those corresponding to HClO<sub>4</sub>. It appears that some of the perchloric acid in HAP is associated with the residual HMB. No perchloric acid was observed at temperatures below 70°C for the treated sample. Neat HAP evolves HClO<sub>4</sub> in quantities easily detected in the mass spectrometer under these same conditions. Hence HMB may be a possible stabilizer for HAP. Concentration effects and other methods for preparing the treated HAP samples need to be determined. (Considerable quantities of ether are absorbed in the oxidizer crystals since even at 100°C large quantities of ether are evolved.)

D. Summary and Recommendation

(U) This phase of the program has accomplished two things: (1) technical information on propellant stabilizer materials and approaches to the problem has been generated, and (2) the treatment of these data has underscored

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TABLE IX-VII

P-BEP INSATURATE SERIES

<u>Material/System</u>	<u>Conditions</u>	<u>Gas Analysis*</u> <u>(ml. <sub>Gas</sub>/g. substrate)</u>	<u>Apparatus Construction</u>
	Temp/Time (°C/decyrs)		
TPT-P-BEP (25 - 50)	80/7	0.8-N <sub>2</sub> ; 0.6-CO; 0.6-CO <sub>2</sub>	Metal system
DPA-P-BEP (25 - 50)	80/7	2.3-N <sub>2</sub> ; 0.3-CO; 0.2-CO <sub>2</sub>	Metal system
TPE-P-BEP (25 - 50)	80/7	0.2-N <sub>2</sub>	Metal system

\* Substrate is P-BEP.

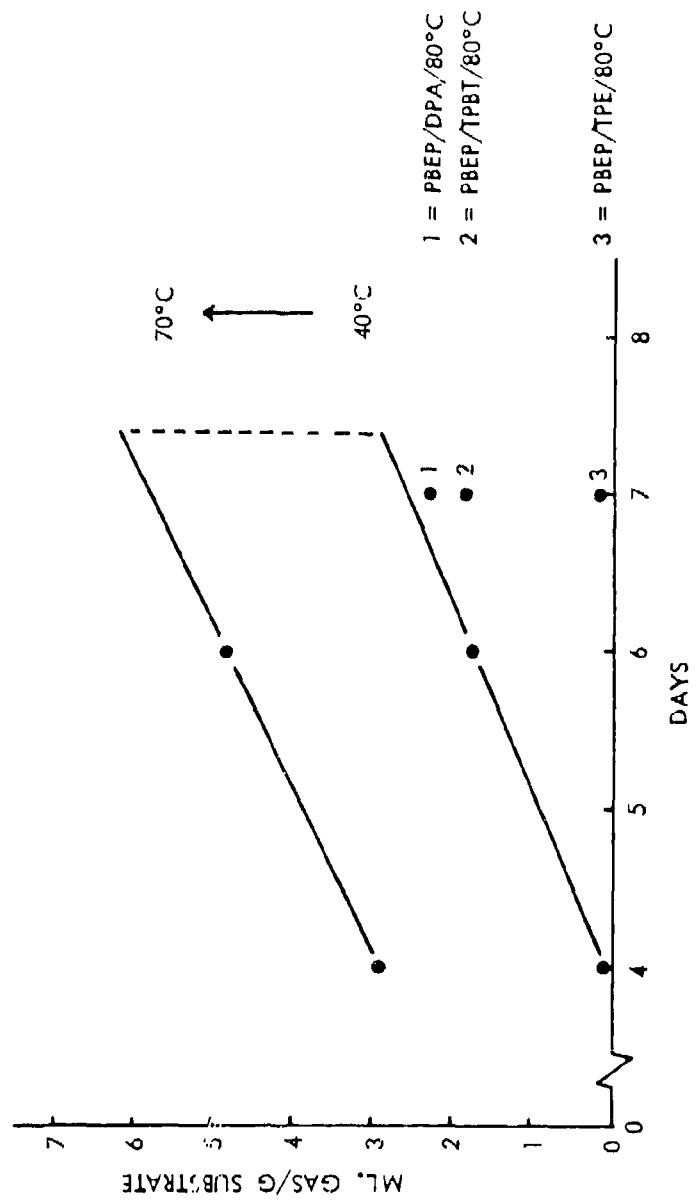


Figure IX-5 - Gas Evolution Envelope for Neat P-BEP Between 40 and 70°C

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the deficiencies in current understanding of stabilization processes and interactions in propellants in general and the NF-hydride system specifically. On the latter point specifically, sufficient knowledge is lacking of the nature of the NF-hydride interaction, the kinetics and energetics of its formation and decay and indeed, whether it is a discrete species or not. Such information is basic not only to effective stabilizer design but is also needed for adequate shelf-life predictions.

In terms of additive materials, HMB is recommended for further development and evaluation as a propellant stabilizer along with the most promising unsaturates, e.g., cyclooctatetraene.

E. References

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3. Varfulomeev, D. F., and V. G. Plyusmin, Dokl. Neftechim Sekts. Baskkir Respub. Pravil. Vses Khim Obshchest., 2, 219 (1966) (Russ.) through C. A., 69400 B (1968). The polymerization of propylene and butenes under influence of HF is accompanied by a number of side reactions: isomerization involving a wide redistribution of H, hydrodehydro-polymerization, and alkyl fluorination. The latter reaction required high concentrations of HF and was dependent on the temperature of the process and nature of the initial olefins.

X.

GLOSSARY OF TERMS

HAP	Hydroxylammonium perchlorate; Thiokol Chemical Corporation, Elkton, Maryland; 97% pure by titration for weak acid.
HP-2	Hydrazinium diperchlorate; Thiokol Chemical Corporation, Brigham City, Utah; 97.8% HP-2.
DOAP	Methylenedioxamine diperchlorate, supplied by RPL.
P-BEP	Poly-bis-difluoraminopropylene oxide; Shell Development Co.
TVOPA	1,2,3-Tris 1,2-bis(difluoramino)ethoxy propane; Rohm and Haas Company.
P-722	2,3-bis(difluoramino)propyl-2,2-dinitropropyl carbonate Shell Development Company.
DDI	Diisocyanate of polymerized vegetable fatty acids; General Mills, Inc.
TDI	Toluene diisocyanate; K & K Laboratories.
CTI	Cyclohexane triisocyanate, supplied by RPL.
ERLA-4221	Alicyclic diepoxy acetate; Union Carbide Corporation.
UTREZ-diol	Hydroxyl-terminated polyisobutylene; United Technology Center.
UTREZ	Carboxyl-terminated polyisobutylene; United Technology Center.
R-45M	Hydroxyl-terminated polybutadiene; Sinclair Petrochemicals, Inc.
Telagen-CT	Carboxyl-terminated polybutadiene; General Tire and Rubber Co.
PU-103-109	Ethylacrylate-acrylic acid copolymer (97:3); Rohm and Haas Co.
PU-105-8003	Ethylacrylate-acrylic acid copolymer (95:5); Rohm and Haas Co.
EMD-590	Carboxyl-terminated polyisobutylene; Esso.
MAPO	Tris-(2-methyl aziridinyl) phosphine oxide; Interchemical Corporation.

HMB	Hexamethyborazine
TCB	B-trichloroborazine
TCMB	B-trichloro-N-trimethylborazine
DPA	Diphenylacetylene
TPE	Tetraphenylethylene
TPBT	Tetraphenylbutatriene
LMH-1	Aluminum hydride
HDY	1,5-Hexadiyne
HNO	Hexyn-3-ol
COT	Cyclooctatetraene

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Security Classification

DOCUMENT CONTROL DATA - R & D

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4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Final Technical Report (1 July 1967 - 1 April 1970)		
5. AUTHOR(S) (First name, middle initial, last name) Ivan C. Smith                            John W. Nebgen Raymond E. Foscante                    A. D. McElroy		
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13. ABSTRACT (C) A number of candidate advanced propellant ingredients were studied with the objective of obtaining definitive information regarding their usefulness in new propellant systems. The research was laboratory based, involved small quantities (generally less than 100 mg.) of the ingredient, and dealt generally with the stability of individual ingredients and with stability-compatibility of two or more components of proposed propellants.		
(C) The ingredients studied include:  Perchlorates--HAP, HP-2, DOAP and AP (for comparison), N-F Materials--P-BEP, TVOPA and P-722 Fuel--AlH <sub>3</sub> , and Numerous state-of-the-art binder prepolymers and curatives.		
(C) The results of this study, in combination with data produced elsewhere on related programs, yielded the following picture of ingredient potential and problems.		
(C) HP-2 - inherent properties of this oxidizer pose serious difficulties for which no solution is apparent. (Concluded on back page.)		

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Solid propellants, Compatibility and stability P-BEP TVOPA Aluminum hydride Hydroxylammonium perchlorate Ammonium perchlorate Hydrazinium diperchlorate Propellant binders Oxidizers						

ABSTRACT (Concluded)

(C) HAP - nominally more tractable than HP-2, this oxidizer has fundamental properties which translate into problems for the propellant formulator, and have cooled enthusiasm for its use.

'C) DOAP - the first few samples of this very new oxidizer were disappointing in stability and compatibility. Improvements are possible.

(C) P-BEP - a very difficult substance in the quality control sense; apparently fundamentally unstable in practice, a feature not readily understood in theory and likely due in large part to the impurity-structure defects of production samples.

(C) P-722 and TVOPA - stable and compatible, with only minimal reservations.

'C) AlH<sub>3</sub> - needs to be better understood, its quality and reproducibility controlled; use hinges on improvement in these areas.

(C) Scavenger and stabilizer studies relative to AlH<sub>3</sub> and P-BEP are encouraging to date, and comprise a part of the basis for optimism about these substances.